7th – 9th July 2010
Electro-Optics and Infrared Conference

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Southampton
Optoelectronics
Research Centre

Chalcogenide Glass for Active and Passive Mid-IR Applications

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SO17 1BJ

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Prescribed by ANSI Std Z39-18

Outline

- Background
- Purification and synthesis
- Optical fibre development
- Active devices in the mid-IR
- Concluding remarks

Optoelectronics Research Centre

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Optoelectronics
Research Centre

- 40 year history beginning from ground breaking work in optical fibers
- Now the largest group in UK (170 staff / PhD students, 65 labs)
- Generates ~50% of our Universities Intellectual Property
- Extensive international industrial and University links
- A worldwide alumni of 600 staff many in senior positions
- A photonics cluster of 11 companies
- 270 Publications/11 Patents per year
- 50 Invited / Plenary talks per year
- Staff includes 3 Fellows of the Royal Society

Primary Research Areas

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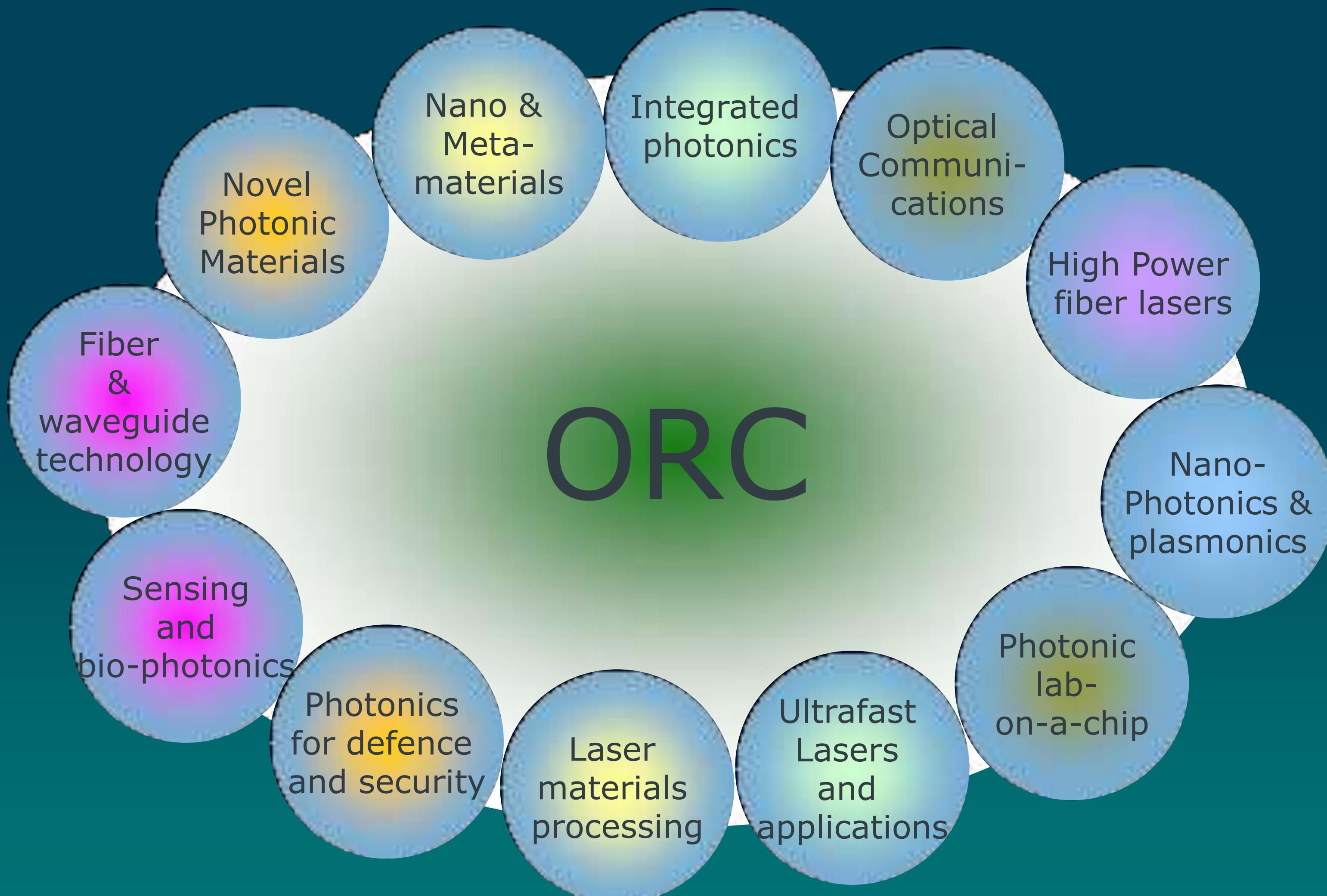

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Purification & Synthesis

- Raw materials
- Reactive gas conversion
- Chemical vapour deposition

Light

The Chalcogenides

What is a Chalcogenide?

- From Greek *sulphur-loving* for elements that frequently bond to sulphur
- Seen in various forms: crystalline, single crystal, quantum dots, phosphors, ceramics

Typical Amorphous Compositions

- As-S, As-S-Se, Ge-Sb-Te
- Predominately As or Se based (toxic!)

ORC Research Focussed On

- Gallium Lanthanum Sulphides (non-toxic)
- Germanium Sulphides (non-toxic)
- Capability to melt any glass composition exists

Glass Melting (Open Atmosphere)

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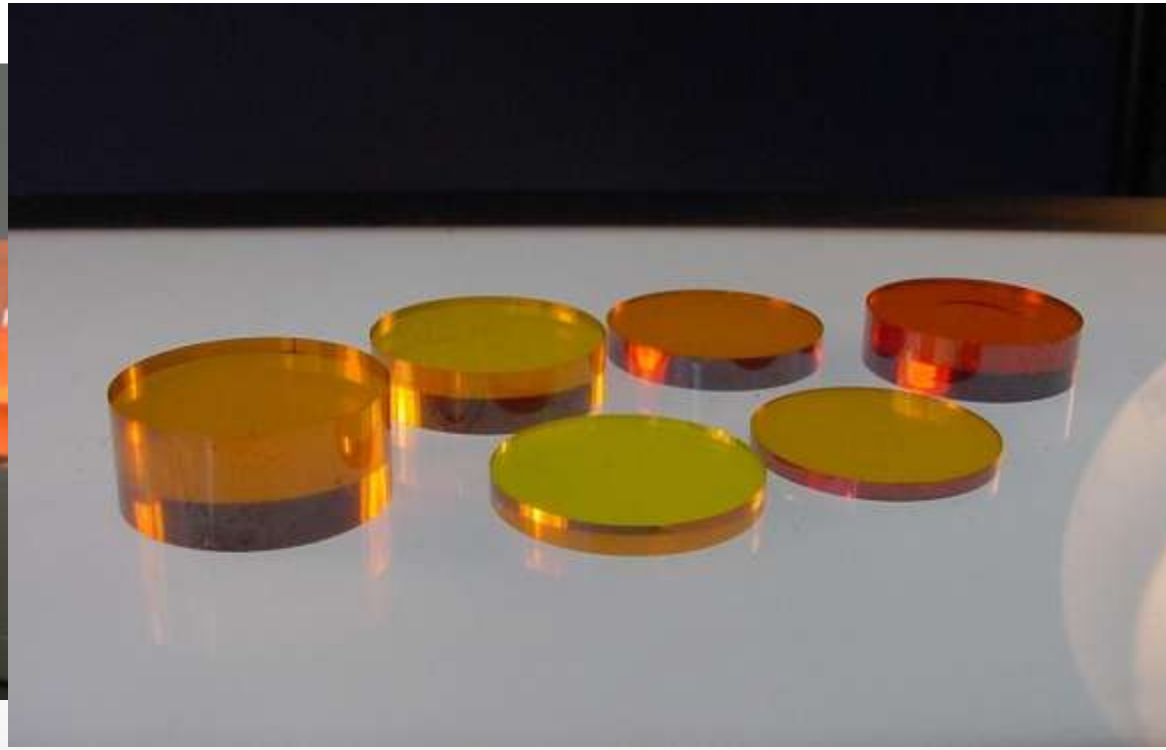
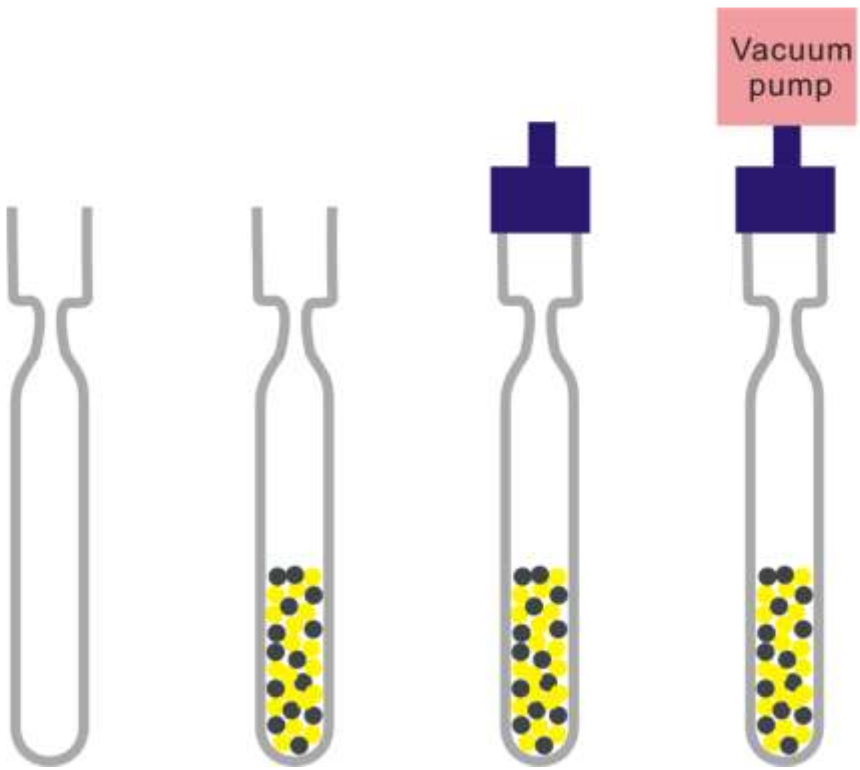



- Wide range of horizontal and vertical tube furnaces, chamber furnaces, high and low temperature ovens, vacuum processing
- Processing in dry nitrogen, argon, oxygen, SF_6, hydrogen and hydrogen sulphide
- Speciality heating including rapid thermal annealing and RF induction

Glass Melting – Sealed Ampoule Melting



Typically used for compounding elements, eg. Ge, Se, Te, Sb

RF Induction Heating

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- Clean, precise, controllable heating
- Custom design, interchangeable coils
- Flexible, we configure the furnace to our needs

CIH_ISM HF20

Up to 20 kW output
50-150kHz

CHELTENHAM INDUCTION HEATING

How Not to Melt Glass

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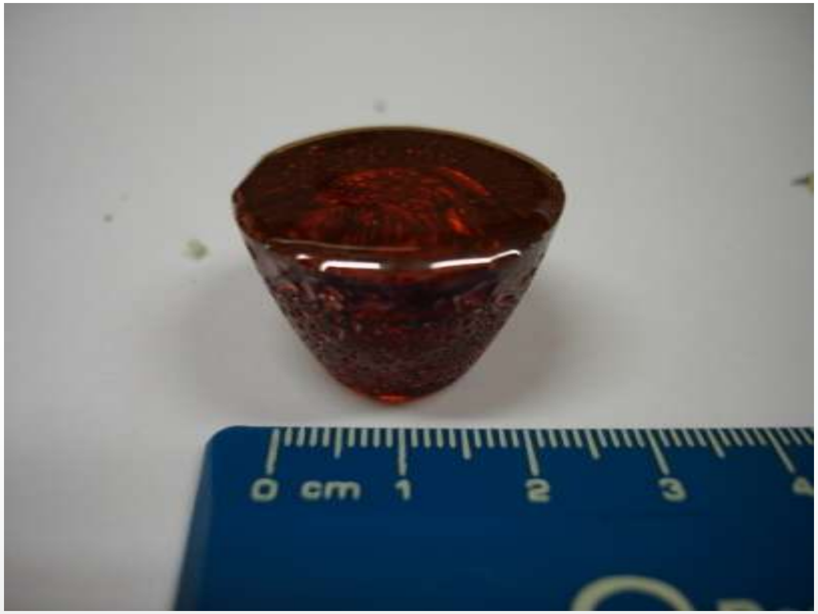
30 October 2005

Raw Materials are Critical!



- Ga-La-S-O samples prepared with mateirals sourced from different manufacturers.
- Melting conditions were identical.

In-House Designed & Built Gas Delivery

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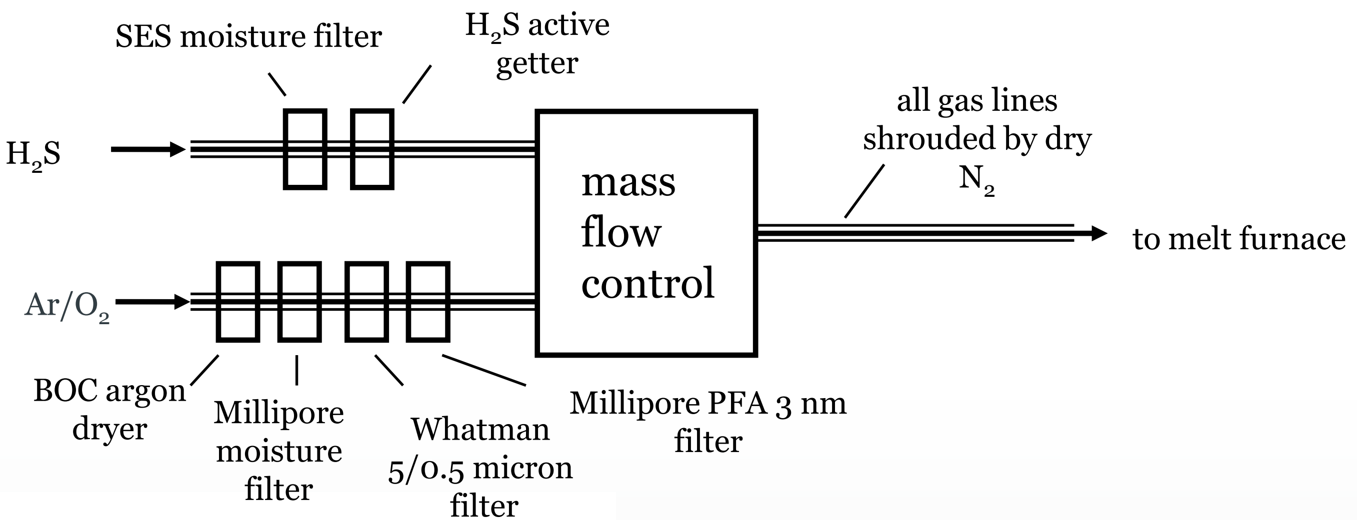
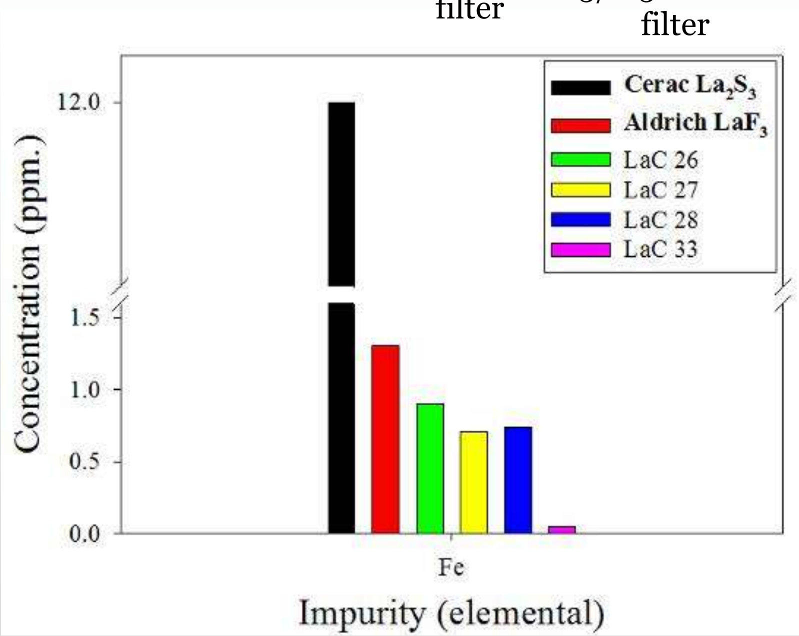
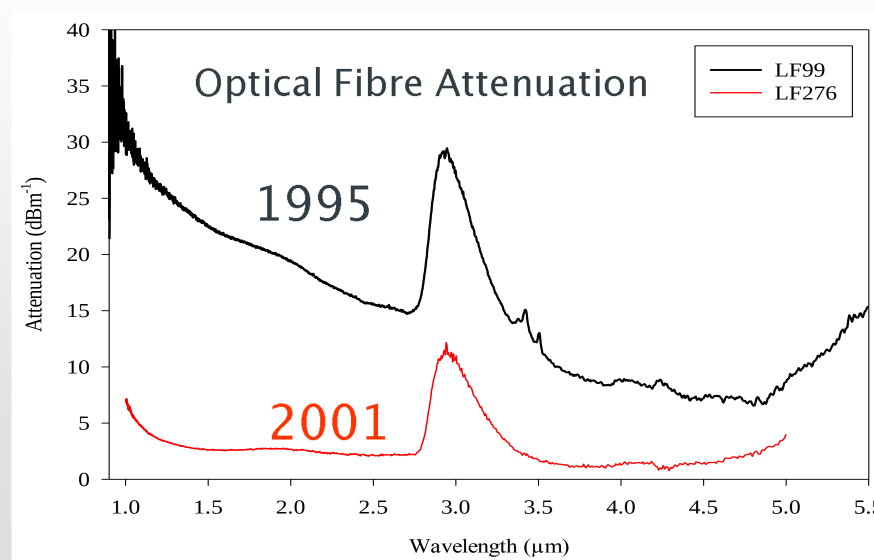
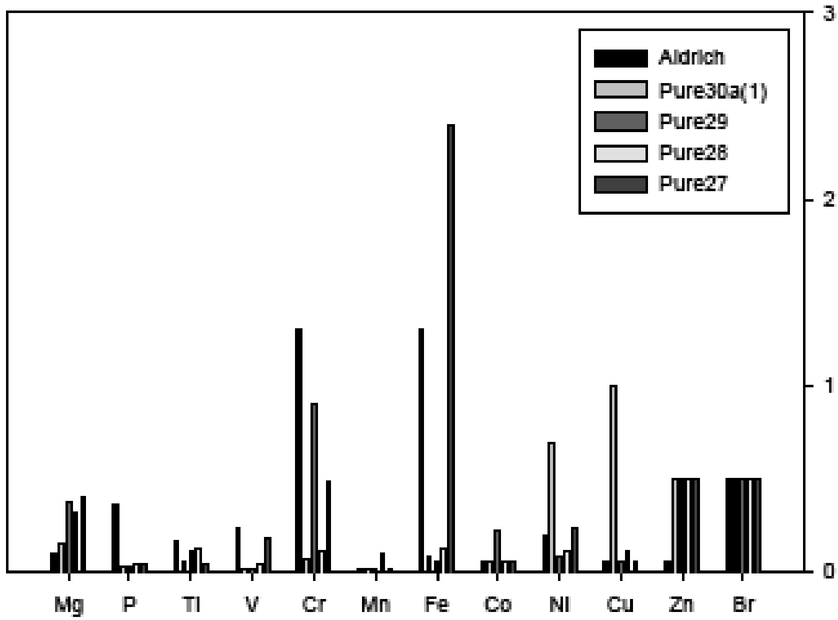


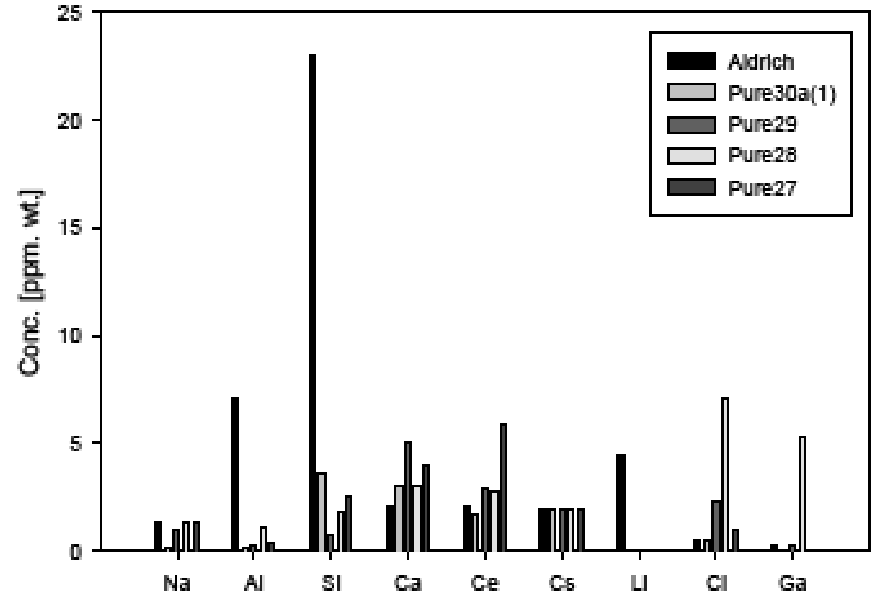




Purity Levels for LaF_3

Aldrich vs In-house purified





Notes

Pure30a(1)
Tube + crucibles baked out = 24hrs. Crucible Type = Ceramic x 2
Tube clean (though used in Pure 30 / LaCO13 / LaCO14). Powder Mass ~ 6g / 8g
Transfer thru use of pod proved impossible.
Crucibles exposed to atmosphere for 1min. Slight black colouring on surface after purification.

Pure29
Crucible Type = Carbon x 2. Powder Mass ~ 20g / 65g

Pure28
Tube + crucibles baked out = 12hrs . New Tube used.
Crucible Type = Carbon. Powder Mass ~ 83g
Appearance of powder after purification = white

Pure27
Tube + crucibles baked out = 12hrs . New Tube used with carbon liner.
Crucible Type = Carbon. Powder Mass ~ 60 / 30g

Purification Run	C	O	S
	(Impurity Content in ppm wt)		
Aldrich	140	400	0.71
Pure30a (1)	70	6000	140
Pure29	43	330	-
Pure28	45	570	160
Pure27	65	210	780

Thermal Properties

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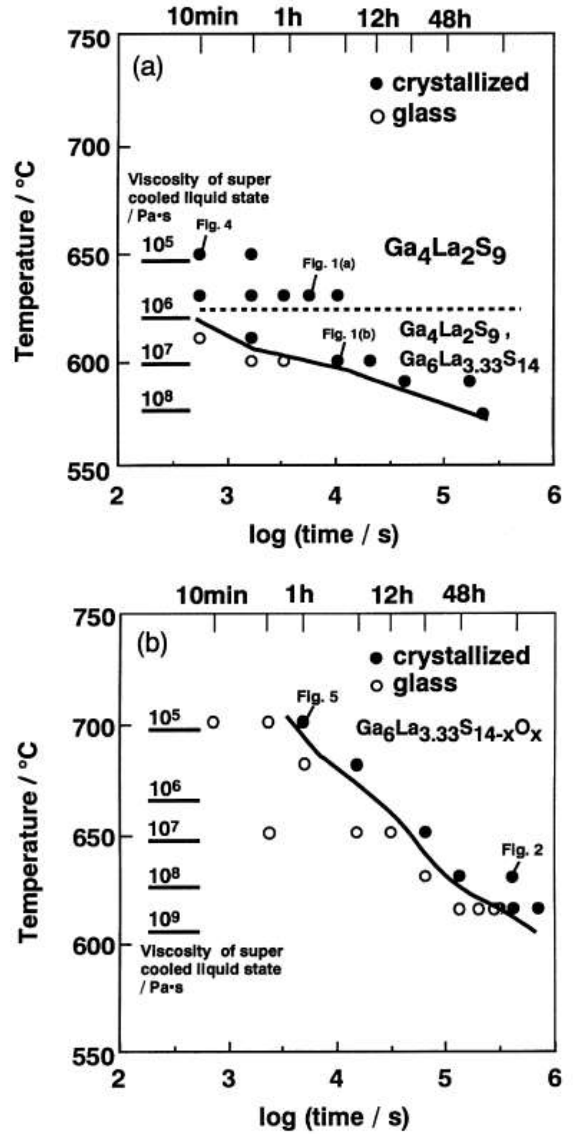

Fig. 3. TTT diagrams of (a) GLS and (b) GLSO glasses during isothermal treatments. Viscosity data of super cooled liquid states is also shown in these figures.

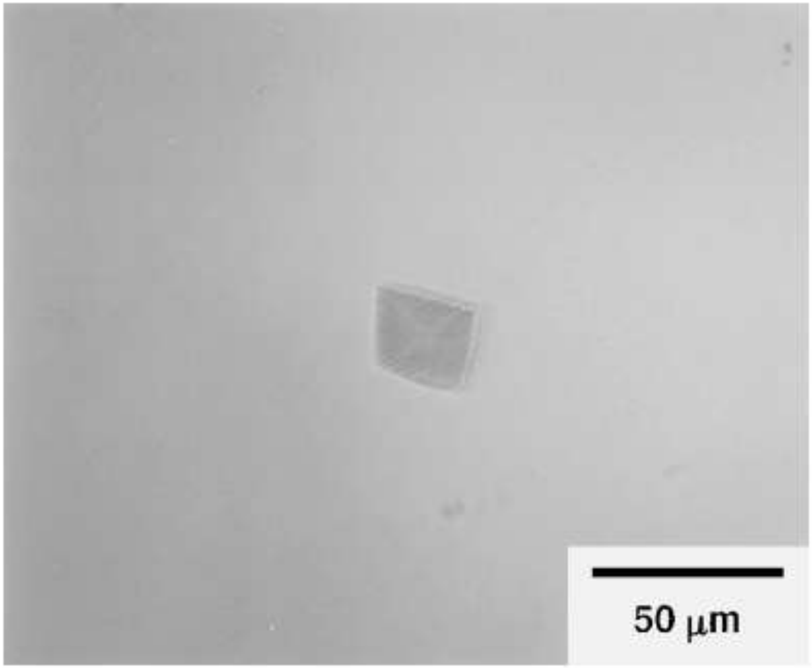

Fig. 5. Transmission optical micrograph of the GLSO glass treated at 700°C for 1 h.

Glass Modification

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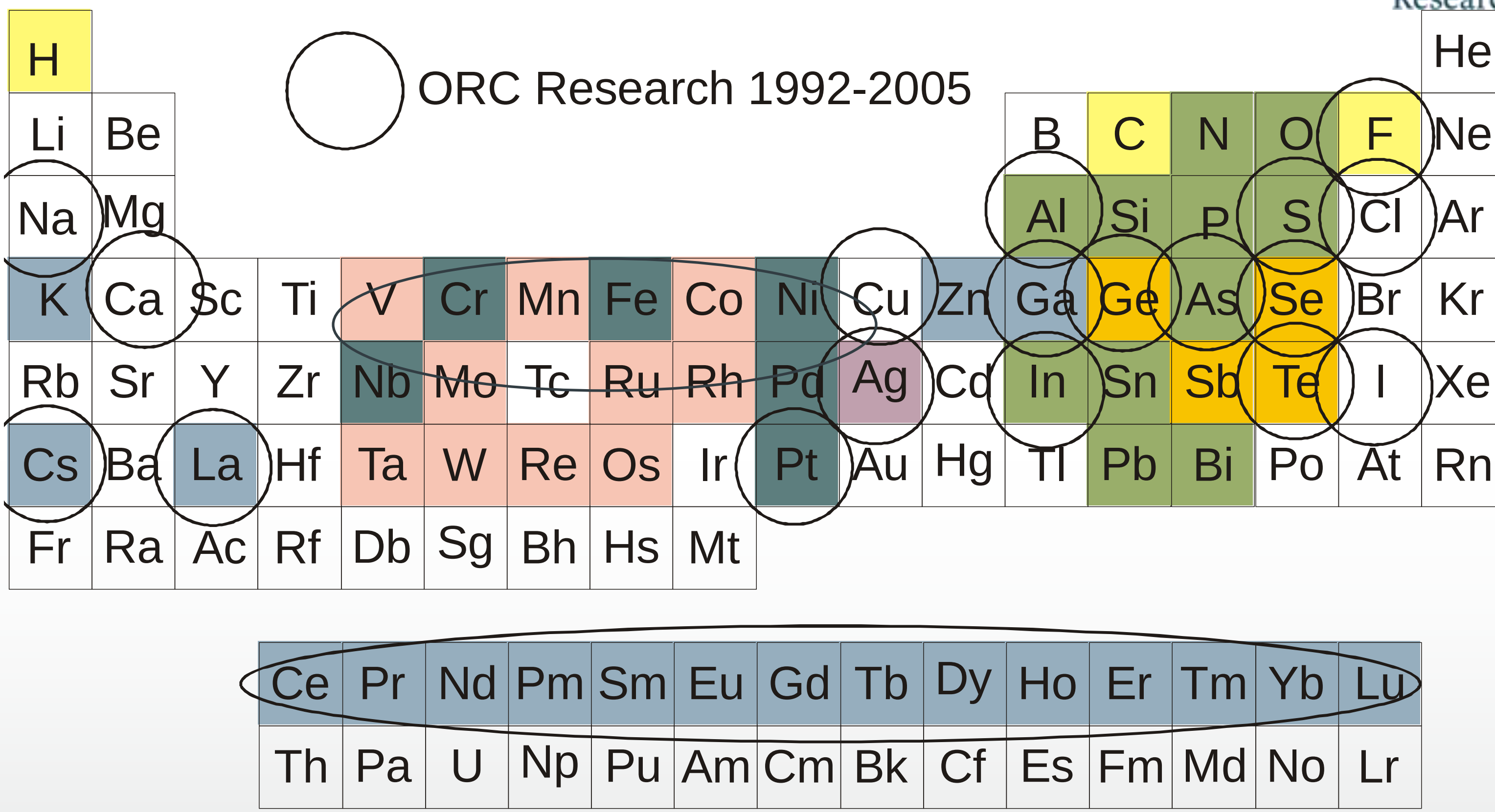

1st Generation US 4115872 ~1978	2nd Generation US 45335219 ~1994	3rd Generation US 5341328 ~1994	4tht Generation US 5406509 ~1995	5th Generation US 6011757 ~2000	Emerging US 4115872 ~2003

Background – Early Mapping of GeSbTe

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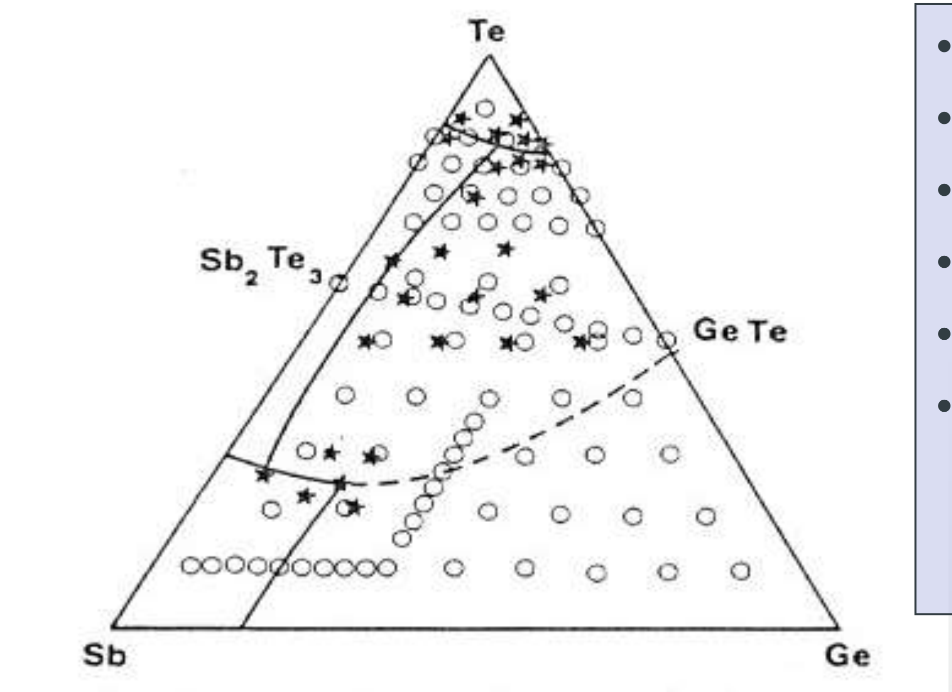


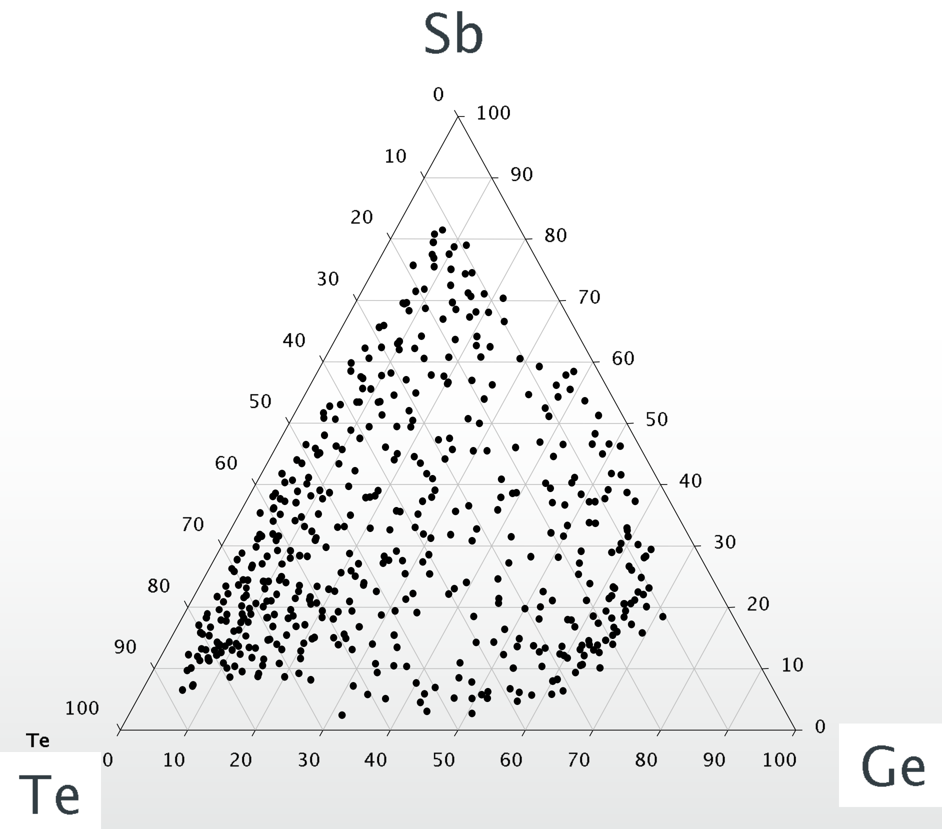
- 100 samples GST alloys studied
- Each melted in sealed ampoules
- Composition individually analyzed
- Melting temperature by DTA
- Tg and crystallization by DSC
- Crystalline phases by XRD

Time Scale: several months?

P. Lebaudy et al, "Identification of amorphous zones in the GeTeSb system", Materials Science and Engineering A132 (1991) 273-276

Full Ternary Analysis

Science-led Materials Discovery



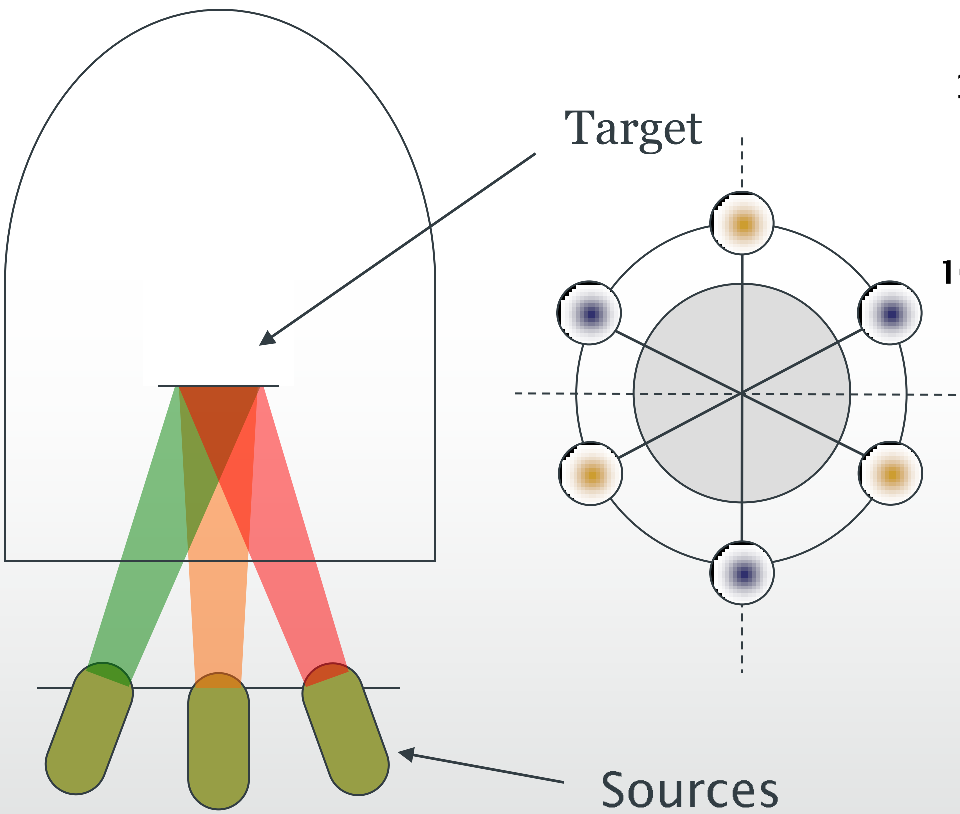
Calibration Runs:	2 - 3 days
Run 653	2 hours
Run 659	2 hours
Run 770	2 hours
Primary Screening	2 - 3 days

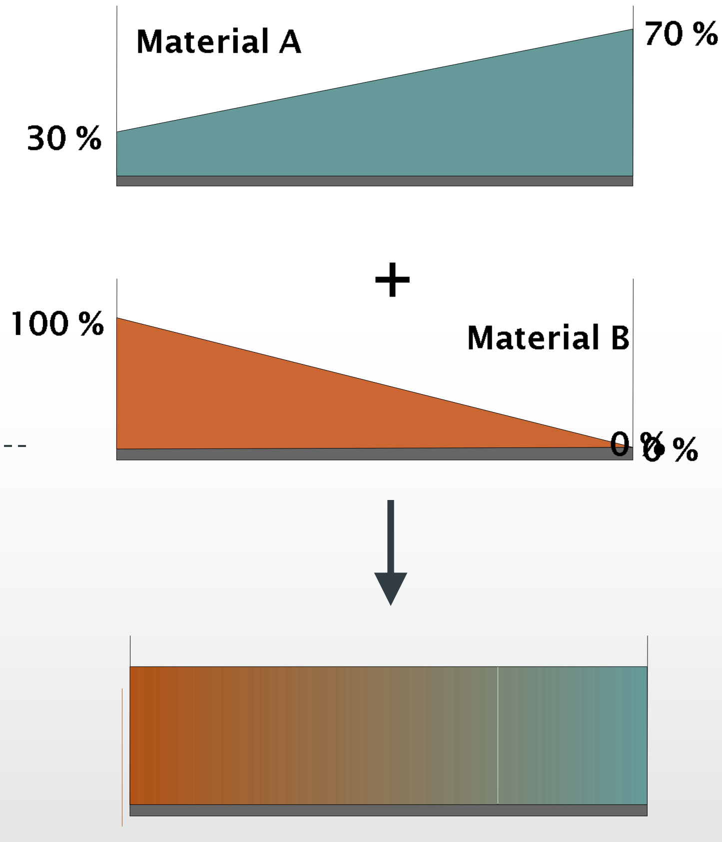
Time Scale: one week

Presented at *EPCOS '05* Cambridge Sep 2005
R.E.Simpson, D.W.Hewak, S.Guerin, B.Hayden, G.Purdy, “High throughput synthesis and screening of chalcogenide materials for data storage”

Pioneering Technology: High Throughput Physical Vapour Deposition
Material Discovery Times accelerated by a factor of 10 - 100

High Throughput Deposition





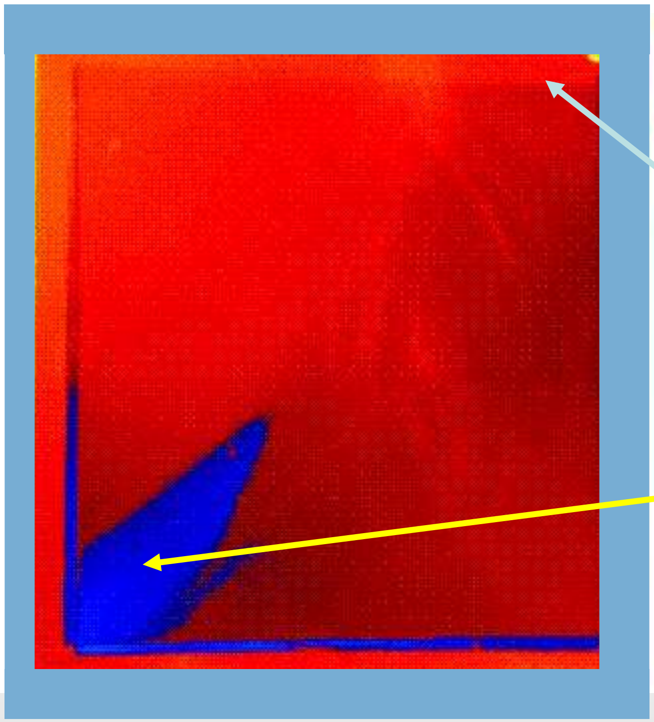
Shutter over each target ensures reproducible and reliable “wedge” which combined gives a desired gradient

Optical Screening

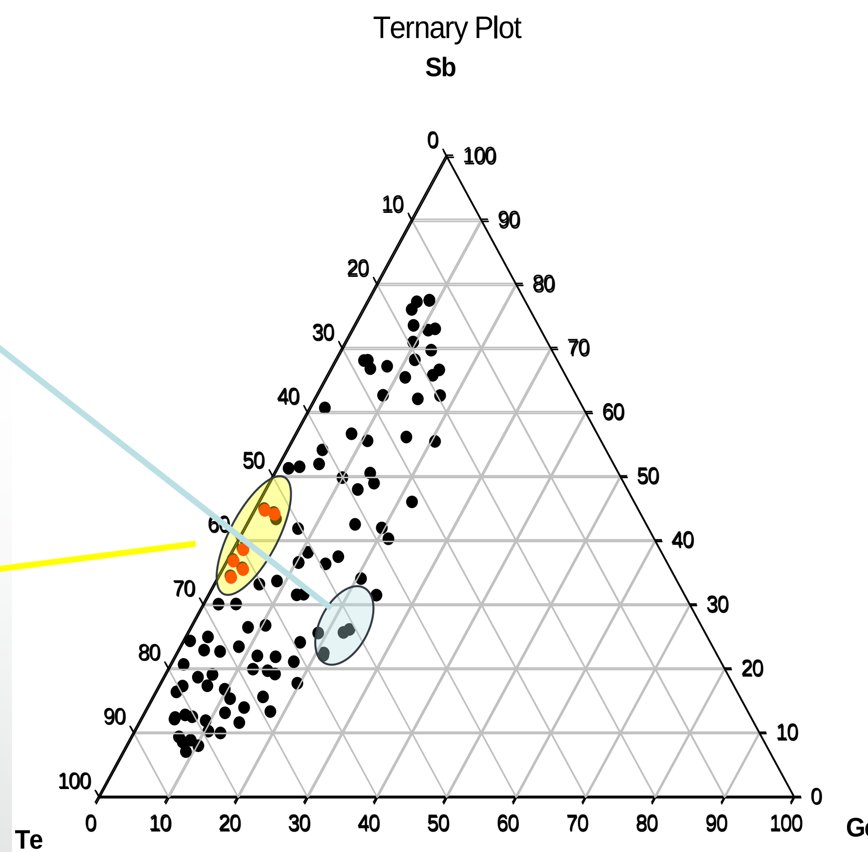
Science-led Materials Discovery

Hot plate heating

25 C

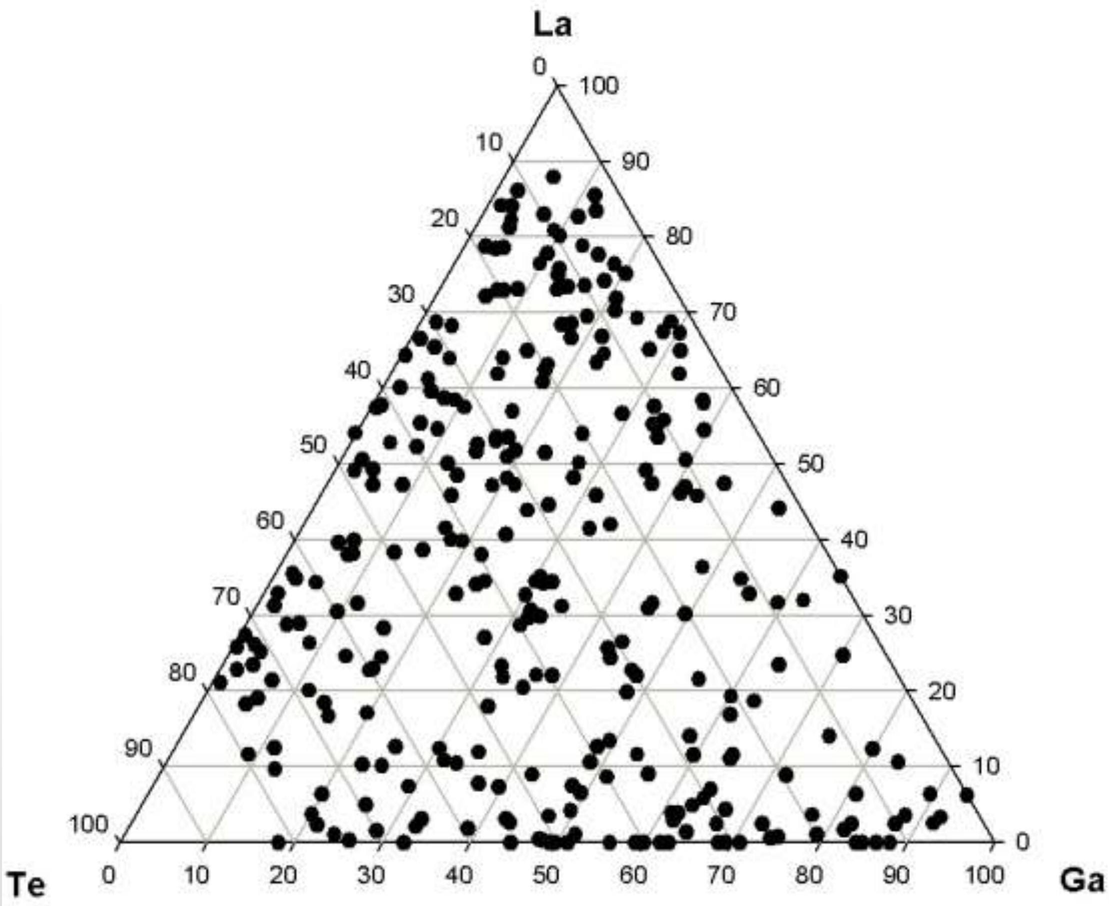


High Sensitivity B&W Progressive Scan
1392 x 1040 pixel CCD Camera
Starlight Express Ltd. Model SXV-H9



Full Compositional Analysis of Ga:Te:La System

EDS 1613 + 1659



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Science-led Materials Discovery

Optical Fiber

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Chemical Vapour Deposition

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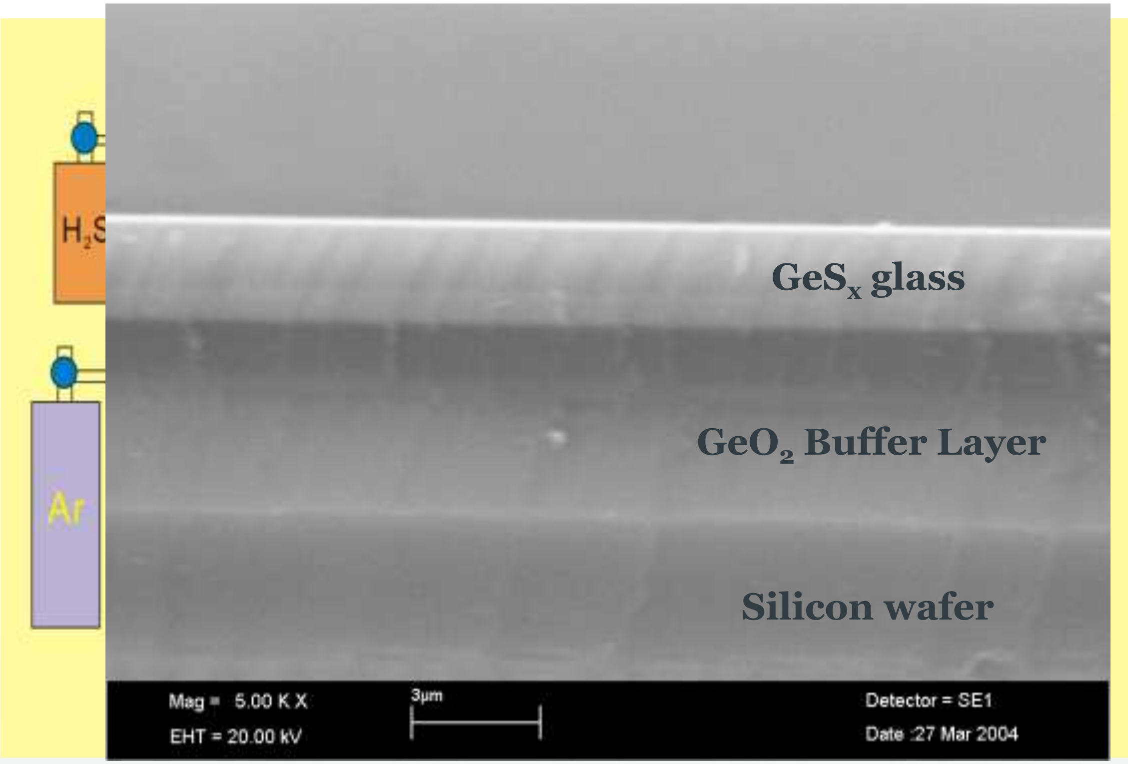
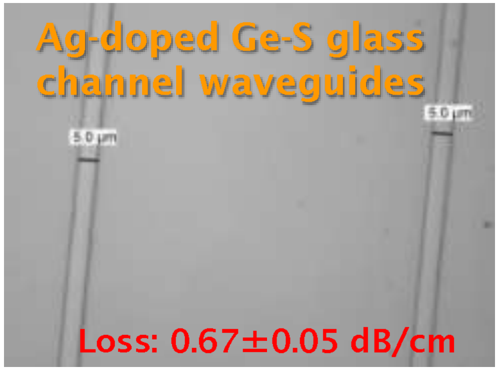
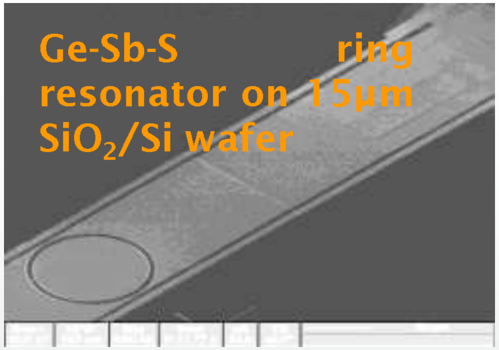
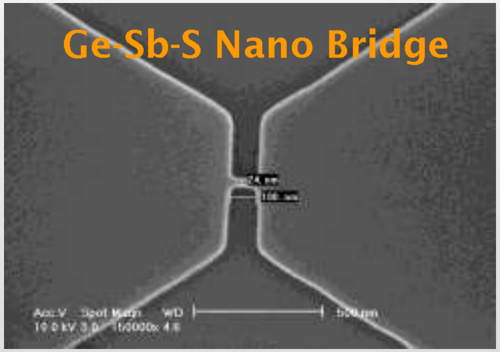




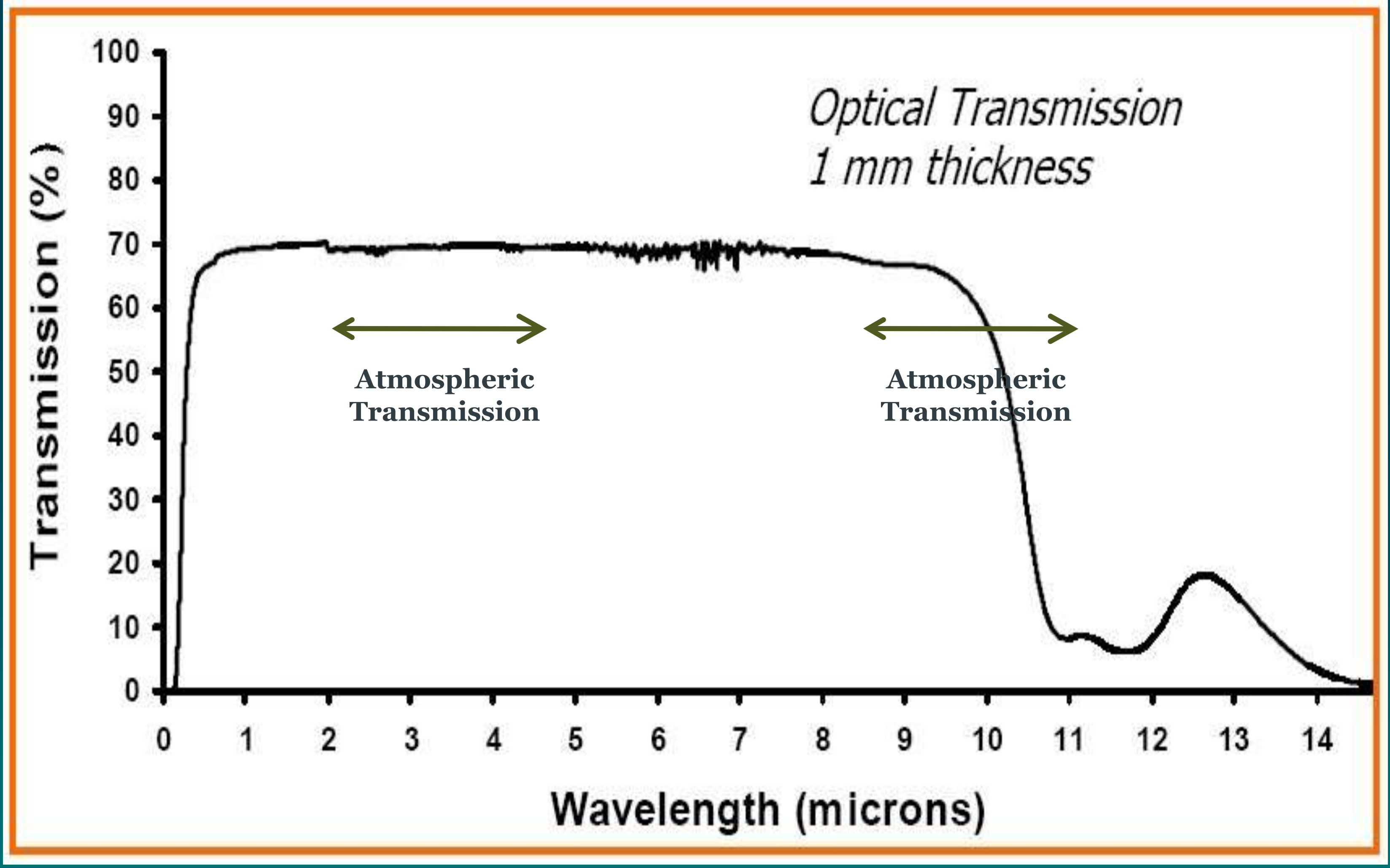




Impurities in glasses prepared by different methods (data in ppm)

Glass	Preparation Method	Cr	Fe	Co	Ni	Cu	Zn
Ge:S	CVD	<0.005	<0.05	<0.05	<0.05	<0.05	<0.05
Ga:La:S	Melt Quench	0.02	0.06	nil	0.04	0.1	<0.5

Optical Transmission



Optical Fibre Results

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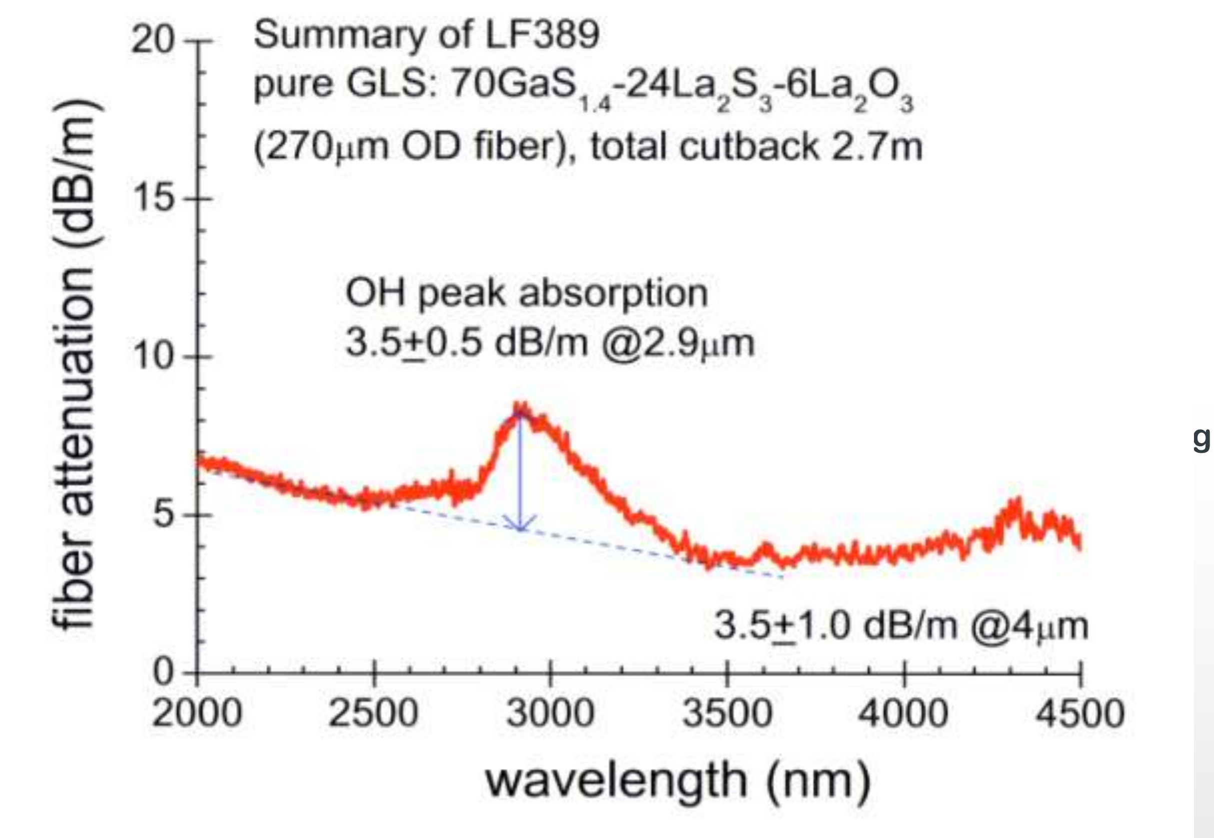
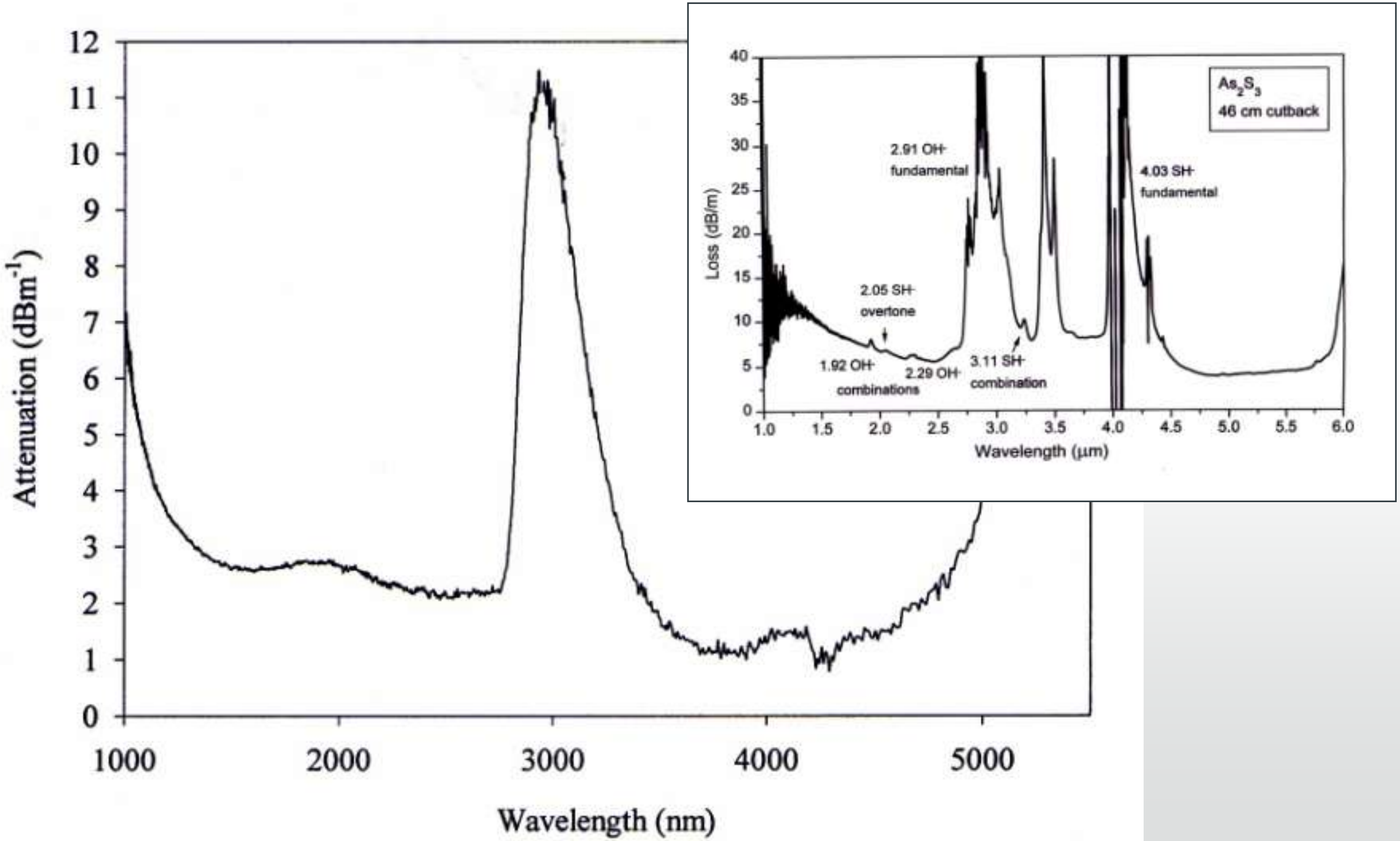


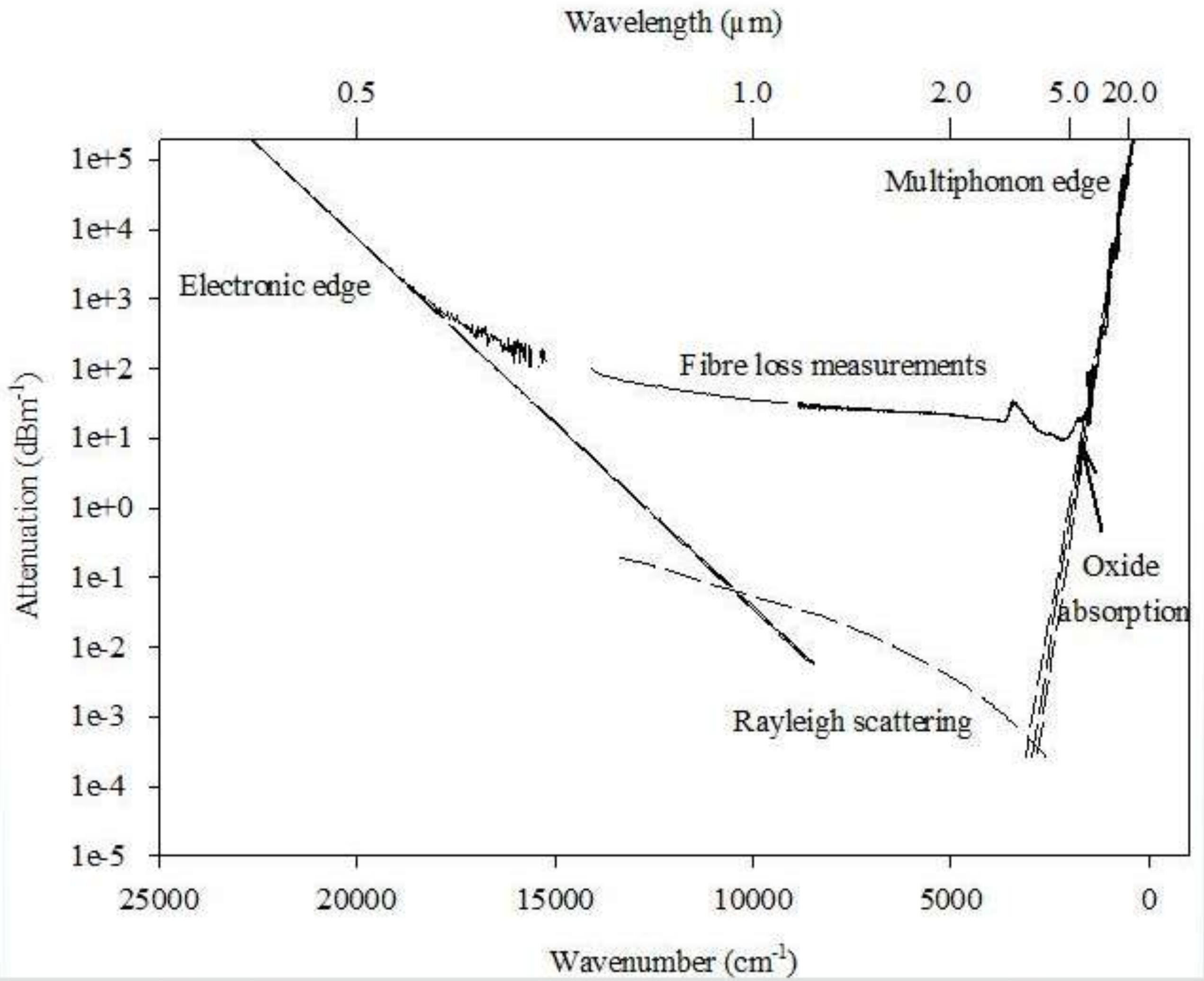
g

	Internal Loss	Optical Fibre
1992	0.1 cm^{-1}	40 – 60 dB/m
2002	0.02 cm^{-1}	2-3 dB/m
Target*	0.004	< 0.2 dB/m

Comparison of GLS fibre with Commercial Arsenic-based fibre



Theoretical Loss Limits



Results in practice are far from predictions!

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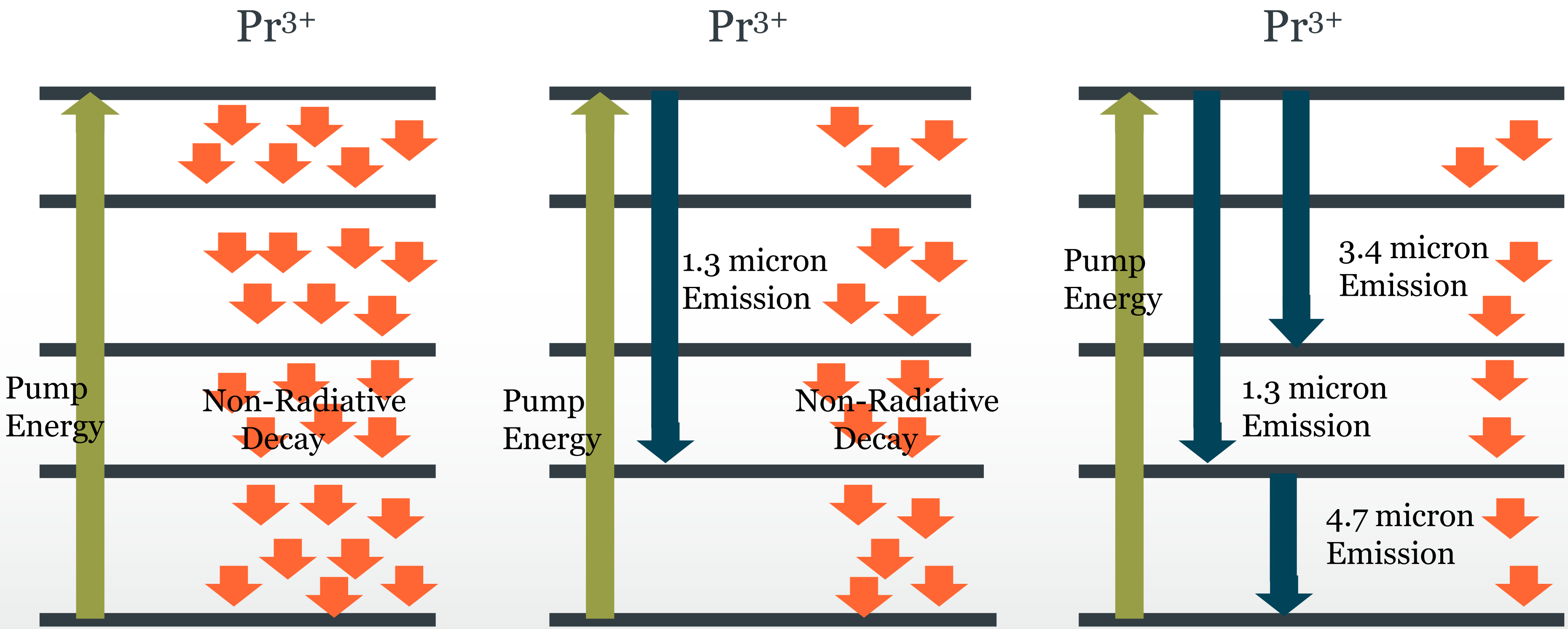
Active Devices

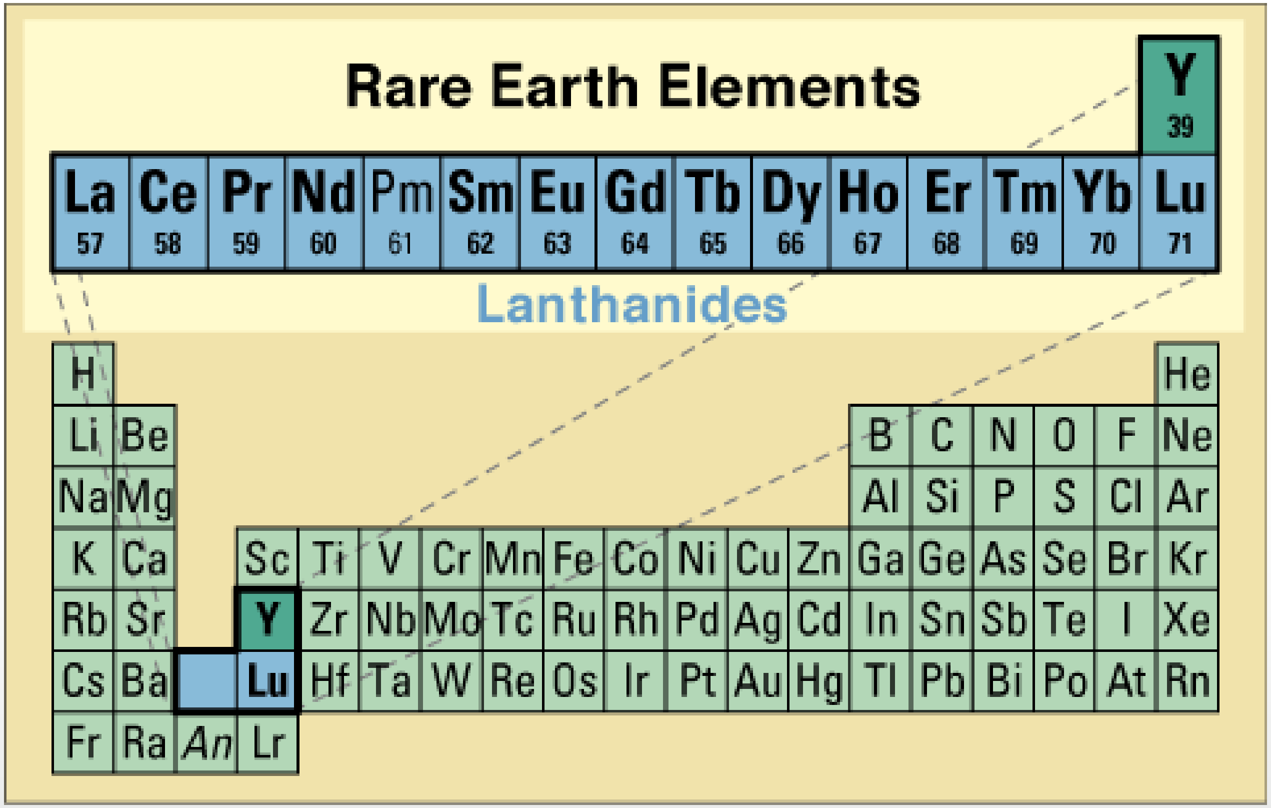
- Mid-IR sources
- Microspheres
- Emerging technologies

Glass Structure & Multiphonon Decay



Oxide Glass	Fluoride Glass	Chalcogenide Glass
High Phonon Energy	Intermediate Phonon Energy	Low Phonon Energy
Efficiency = 0%	Efficiency = 6%	Efficiency = 60%

Rare Earth Doping



T. Schweizer, *Rare-earth-doped Gallium lanthanum sulphide glasses for mid-infrared fibre lasers* (University of Southampton, 2000)

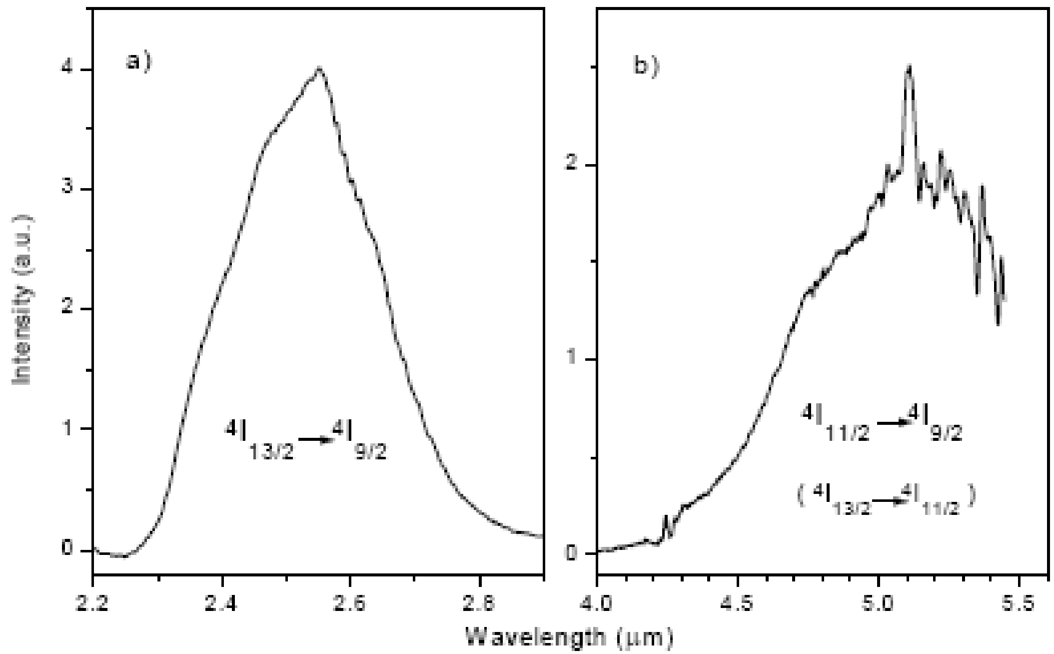


Fig. 6 Emission from the two lowest Nd^{3+} levels, $^4I_{13/2}$ (a) and $^4I_{11/2}$ (b), in 1.5 mol% Nd_2S_3 doped GLS glass pumped at 815 nm with a Ti:sapphire laser and measured with a 300-mm monochromator and a liquid nitrogen cooled InSb detector

Nd^{3+}

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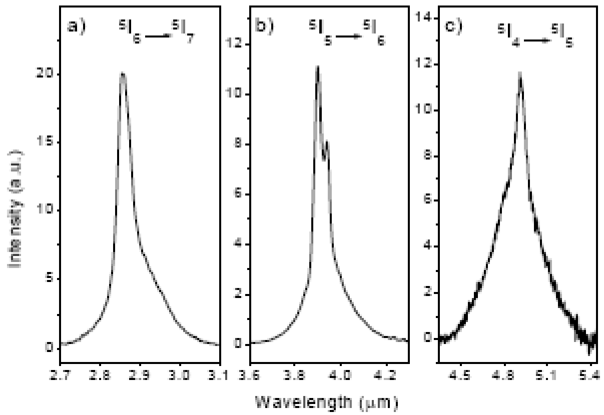


Fig. 5 Mid-infrared emission a) from the $^5I_6$ level, b) from the $^5I_5$ level, and c) from the $^5I_4$ level in Ho(1.5%):GLS pumped at 0.76 μm

Ho^{3+}

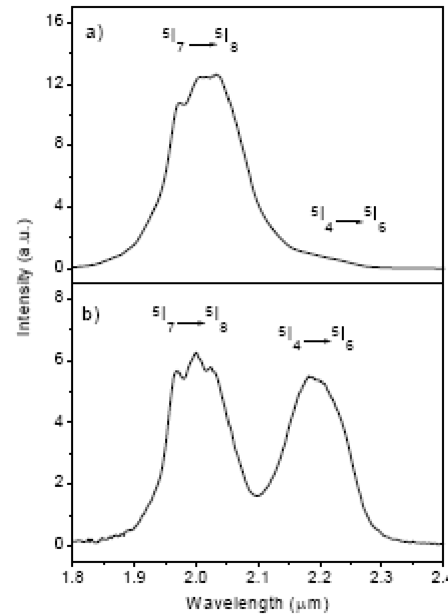


Fig. 3 Overlapping emission at 2.0 and 2.2 μm from the $^5I_7$ and the $^5I_4$ levels in Ho(1.5%):GLS pumped at 0.76 μm
a) continuous wave pump laser
b) pump laser chopped at 400 Hz

Tm^{3+} and Er^{3+}

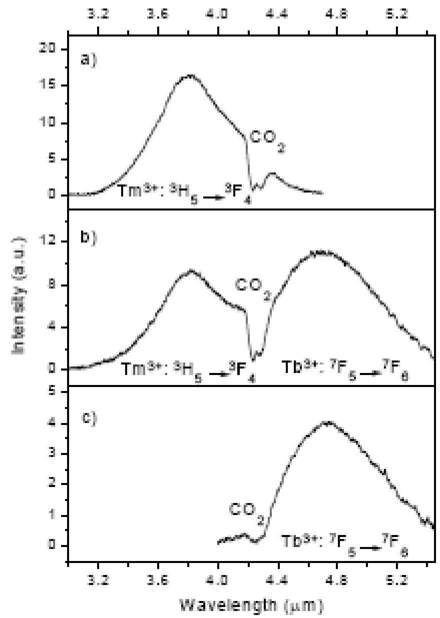


Fig. 7 Uncorrected fluorescence spectra of
a) Tm(1.5%):GLS glass pumped at 0.7 μm
b) Tm(1.5%),Tb(0.2%):GLS glass pumped at 0.7 μm
c) Tm(1.5%),Tb(0.2%):GLS glass pumped at 2 μm

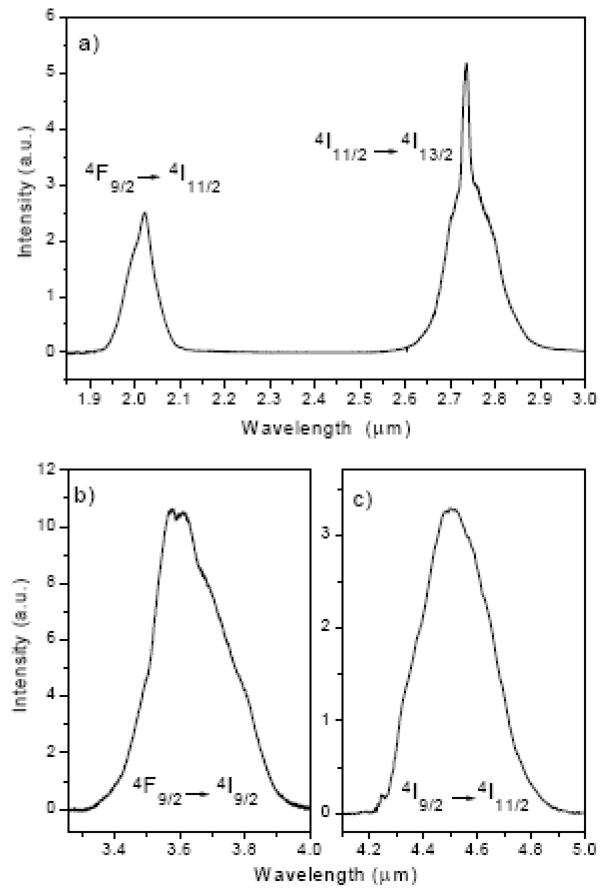


Fig. 4 Fluorescence spectra of 1.57 mol% Er^{3+} doped GLS glasses and fibres
a) 2.0 μm and 2.75 μm emission from 3.9 cm of 270 μm diameter fibre pumped with 60 mW at 660 nm
b) 3.6 μm emission from 8.6 cm of 270 μm diameter fibre pumped with 70 mW at 660 nm
c) 4.5 μm emission from a bulk glass sample pumped with 570 mW at 810 nm

Pr^{3+}

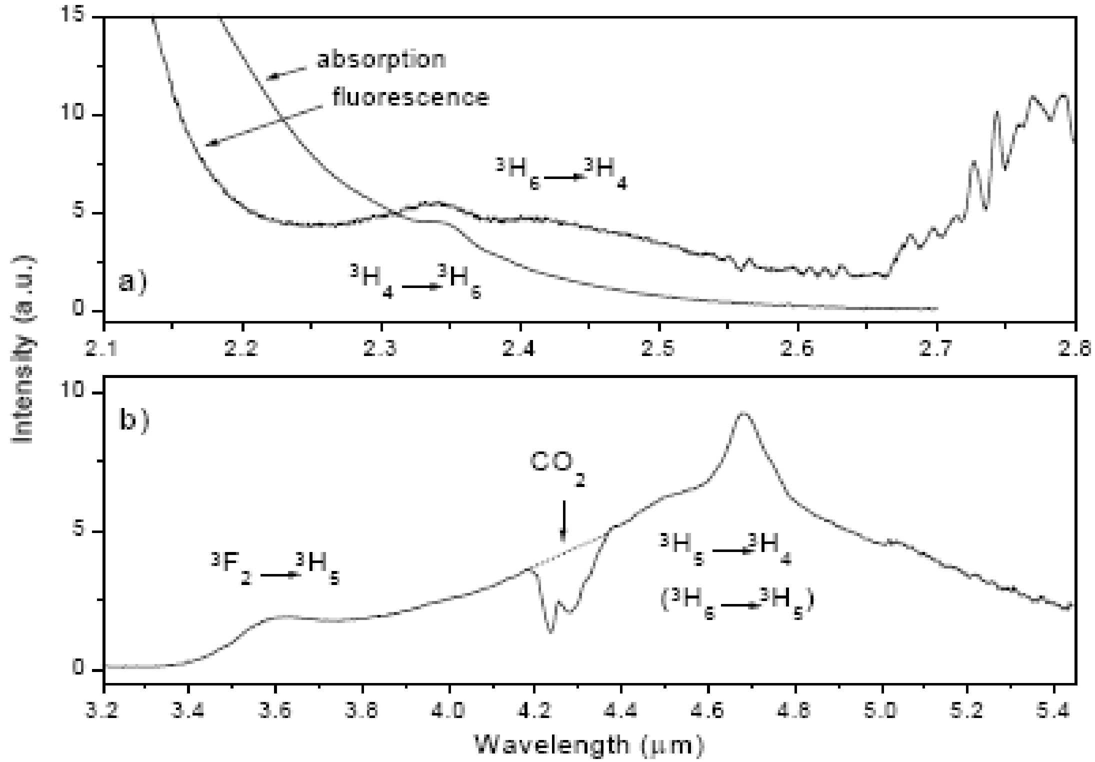
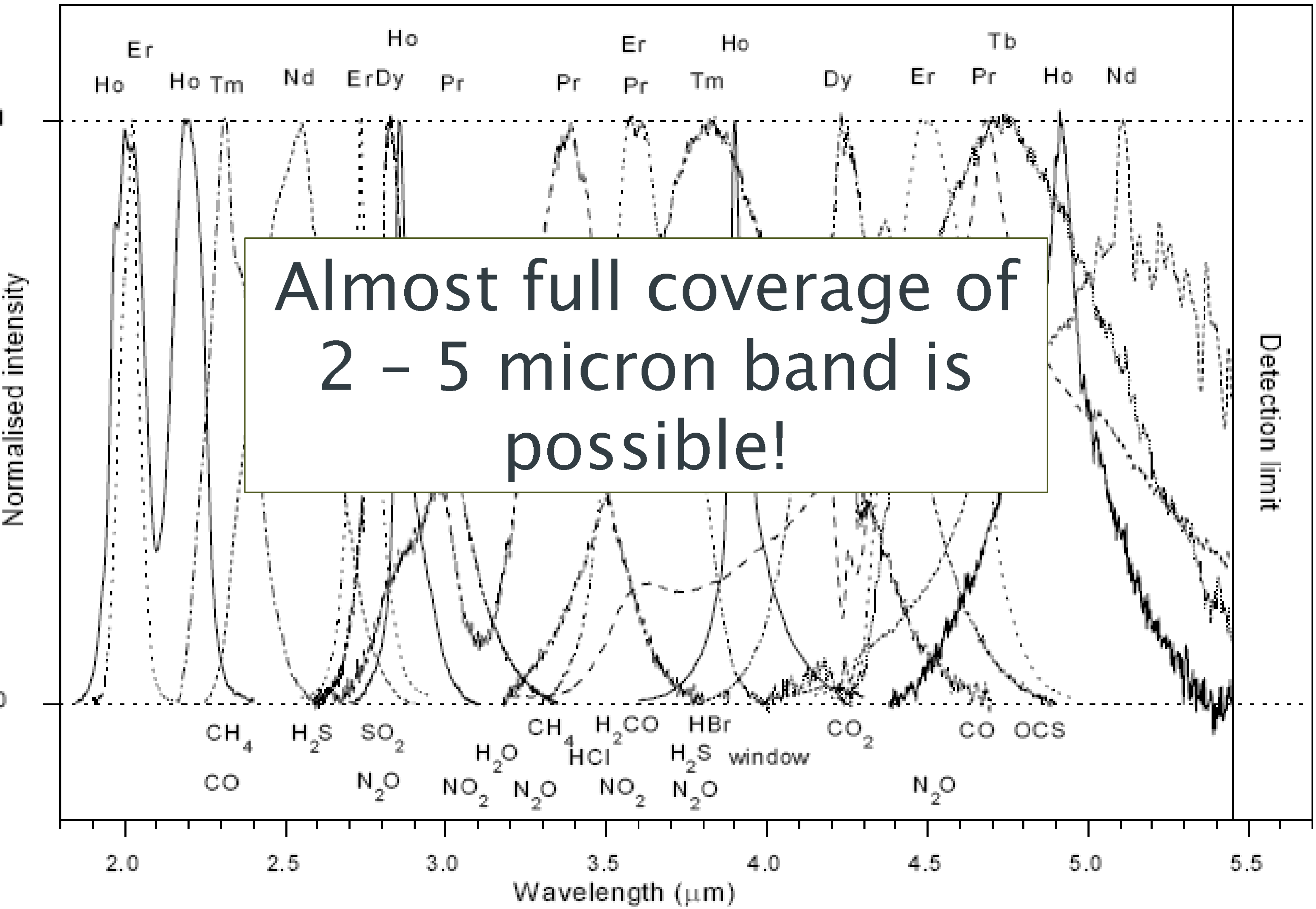


Fig. 3.4.4 Emission from three lower Pr^{3+} levels:
a) Fluorescence from 2 m long, 500 ppm Pr^{3+} doped GLS fibre pumped with 1.064 μm Nd:YAG laser and absorption spectrum
b) Fluorescence from 2000 ppm Pr^{3+} doped GLS bulk glass pumped with 2 μm Tm:YAG laser



Almost full coverage of 2 – 5 micron band is possible!

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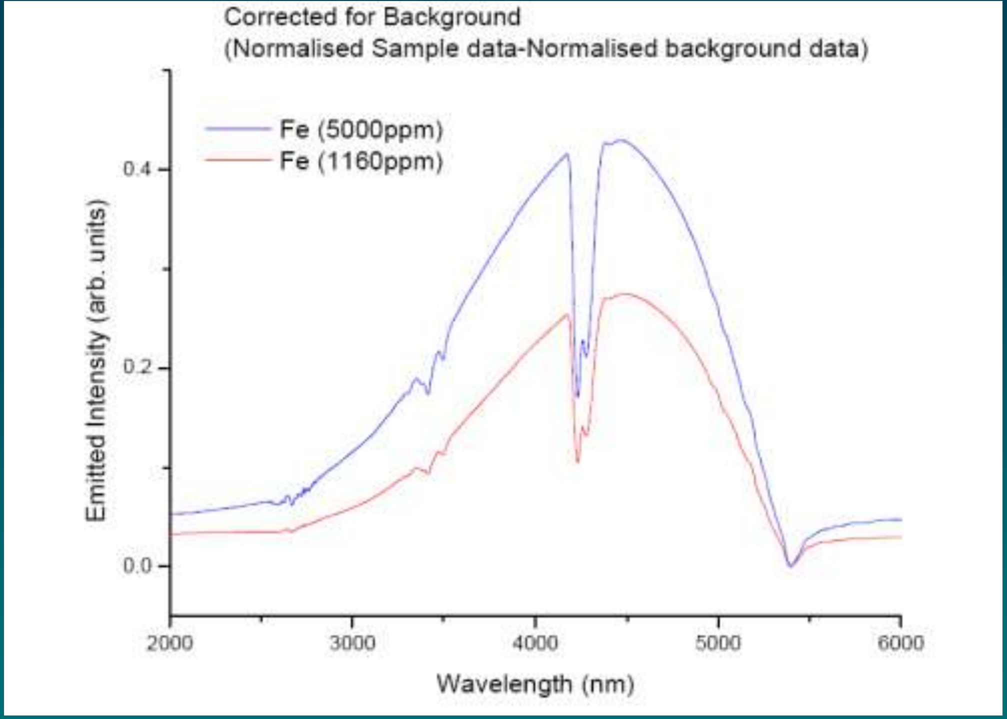
Transition Metal Doping

IIIB	IVB	VB	VIB	VIIB		VII		IB	IB
21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn



Direct Emission Mid-IR Lasers

Research Contract from UK Laser Coalition
DSTL, Qinetiq, BAe Systems, Selex

Microspheres

Microsphere Fabrication

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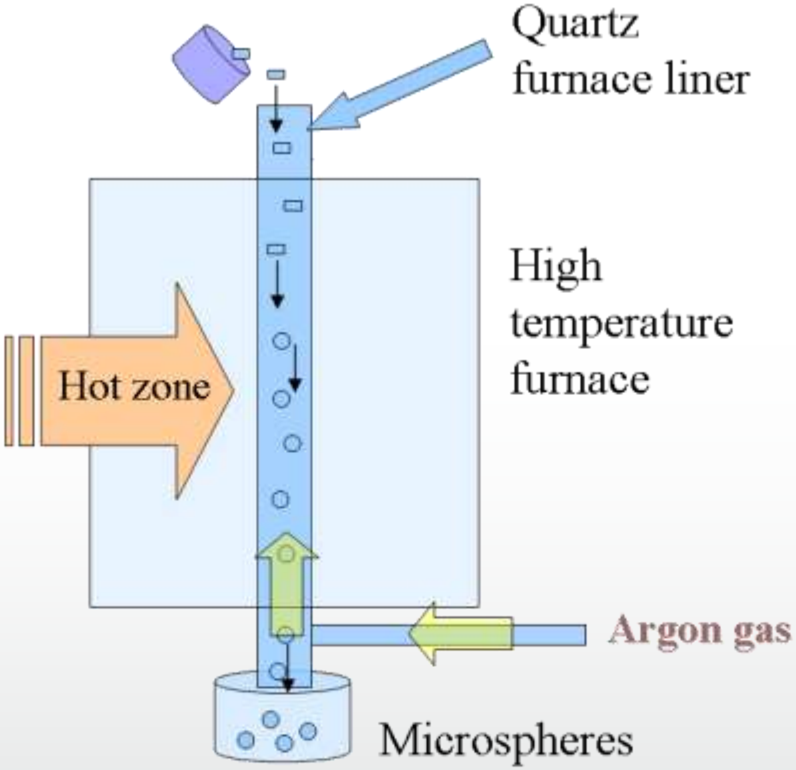

Microsphere diameters 500 nm to 500 µm

Sphere Sorting

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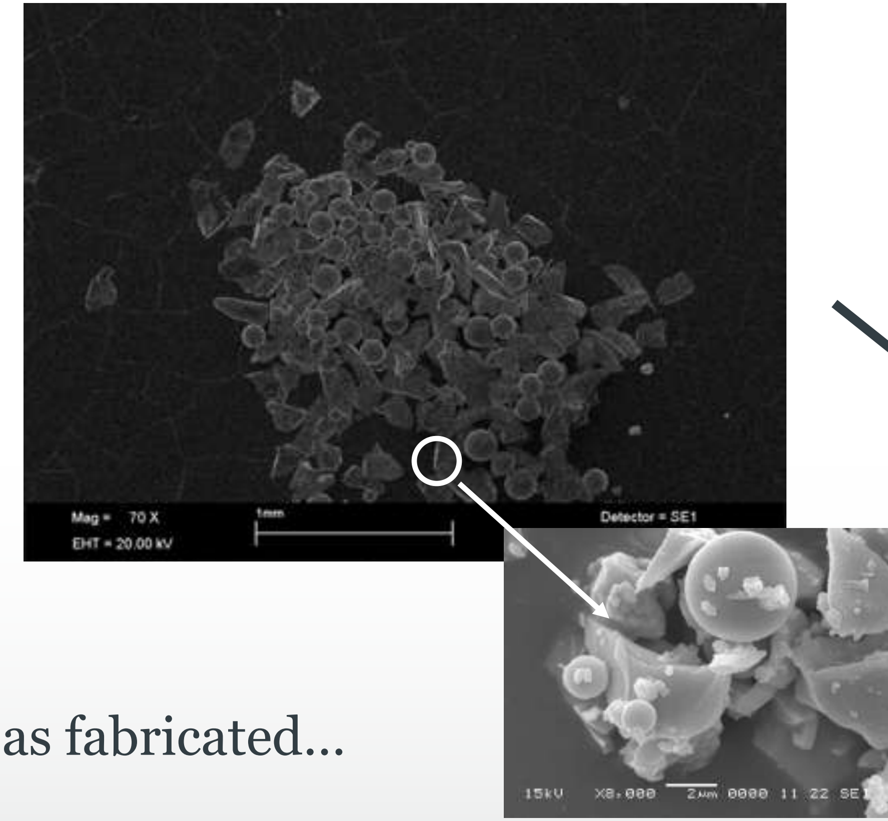
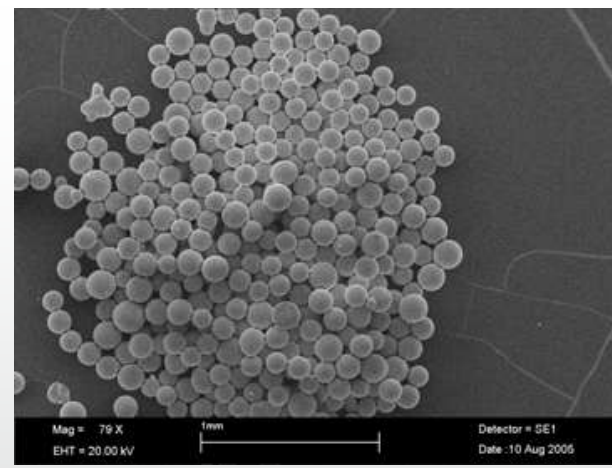
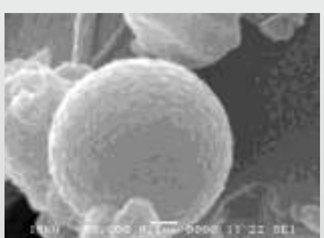


as fabricated...

sieving
sedimentation
rolling





Size range:
100’s nm to 100’s microns

Greg Elliott

Microsphere Characterization

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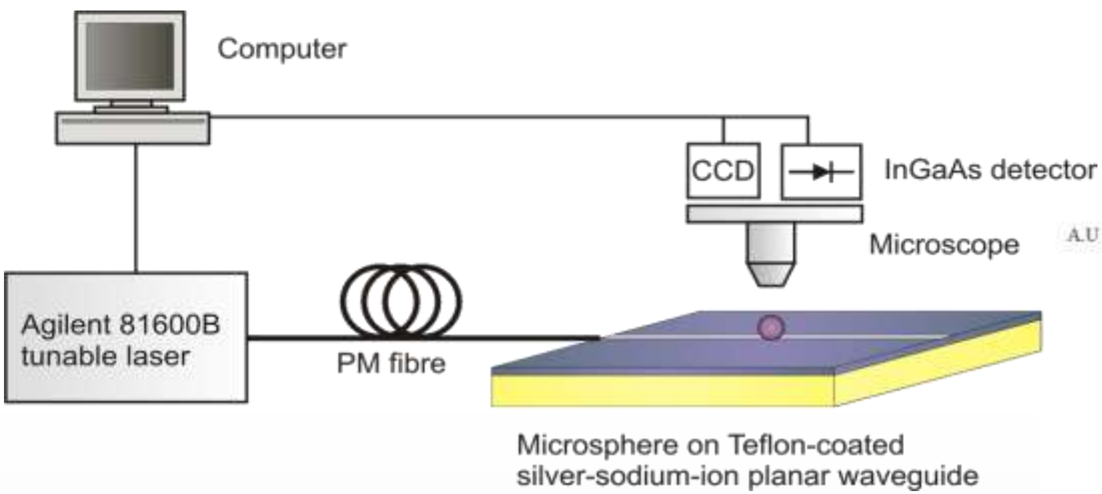
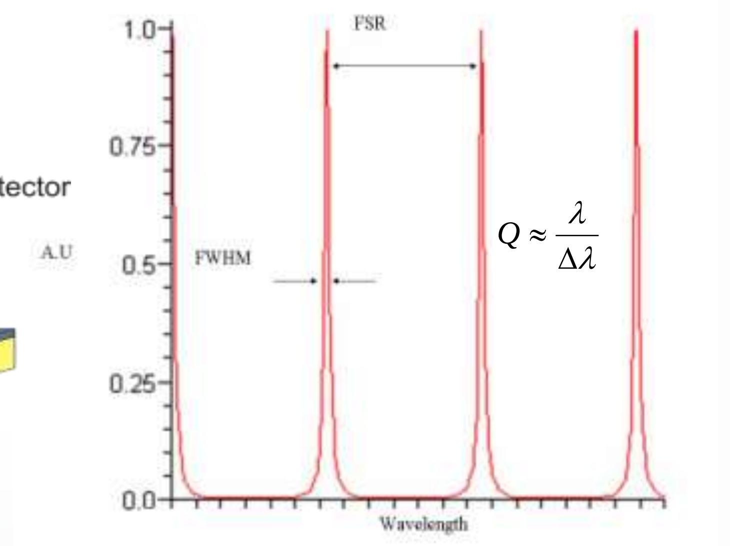


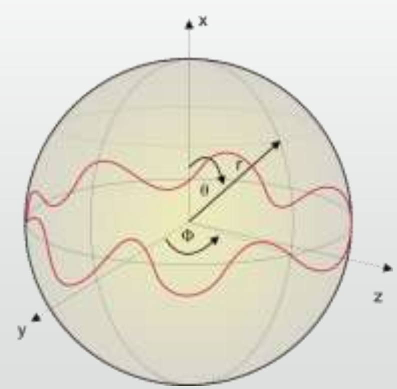


Quality Factor: Q where $1/Q = 1/Q_{material} + 1/Q_{surface} + 1/Q_{curvature} + 1/Q_{coupling}$

$Q_{predicted} = \sim 4 \times 10^9$

$Q_{measured} = 8 \times 10^4$

Gregor R. Elliott, Daniel W. Hewak, G. S. Murugan, and James S. Wilkinson, "Chalcogenide glass microspheres; their production, characterization and potential", Optics Express, Vol. 15, Issue 26, pp. 17542-17553



Improved Coupling

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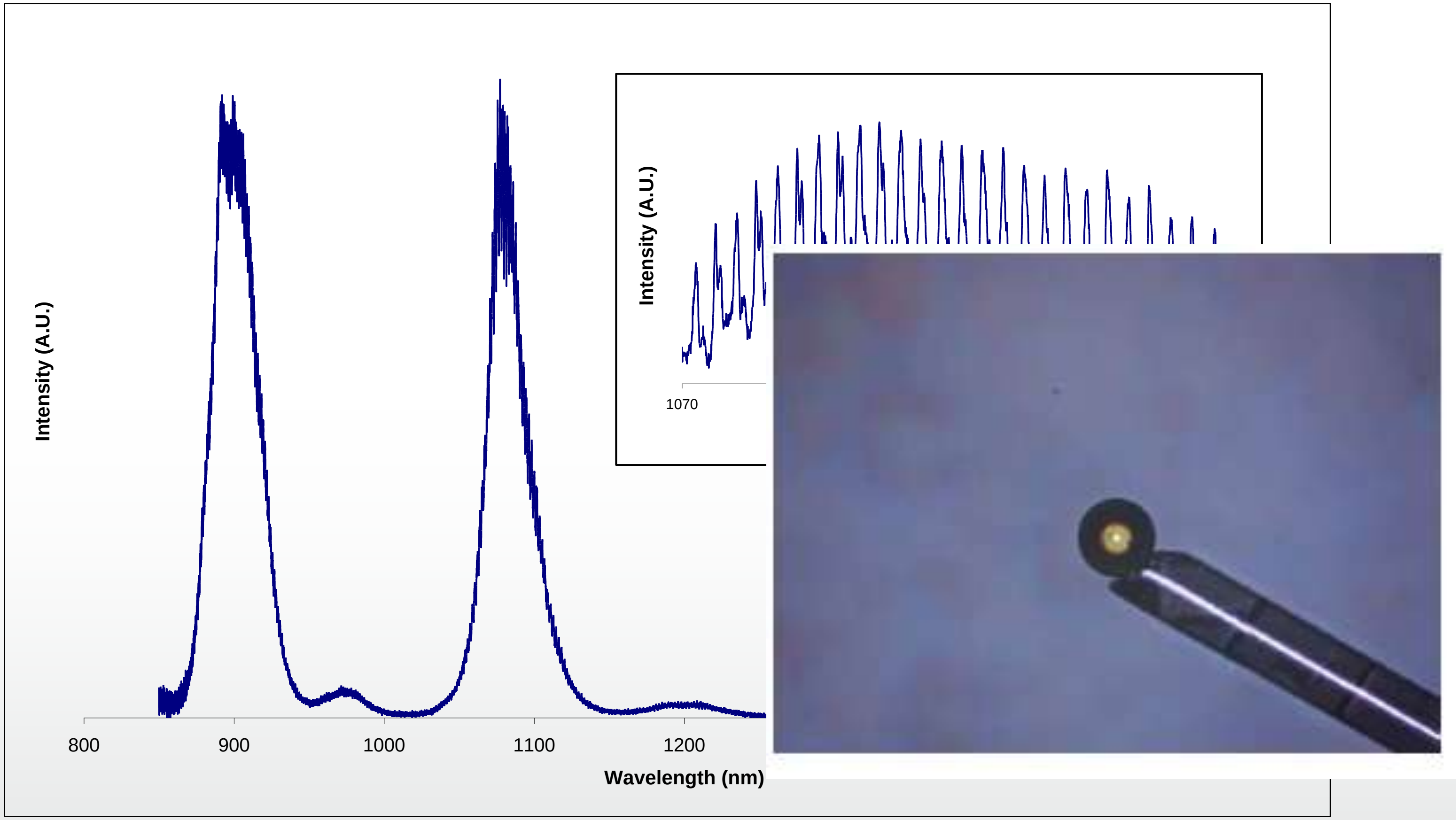
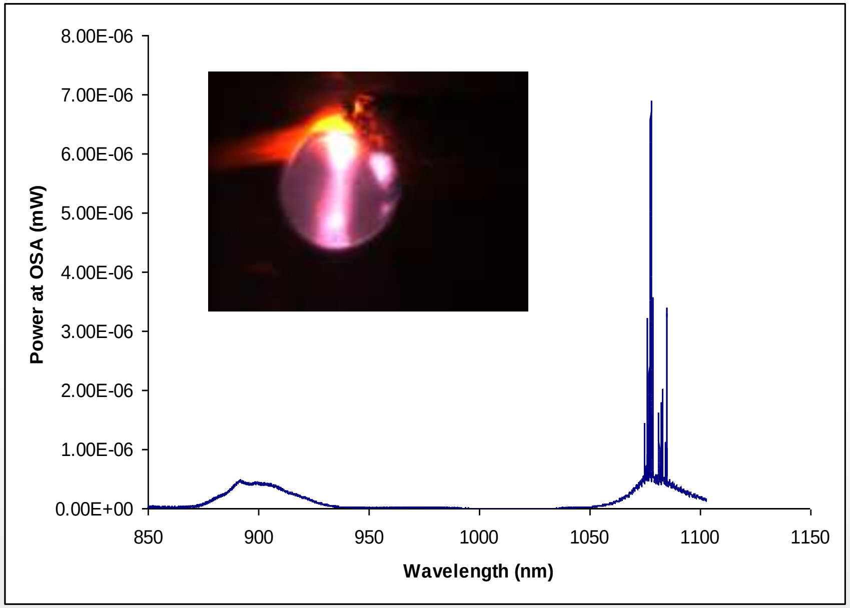
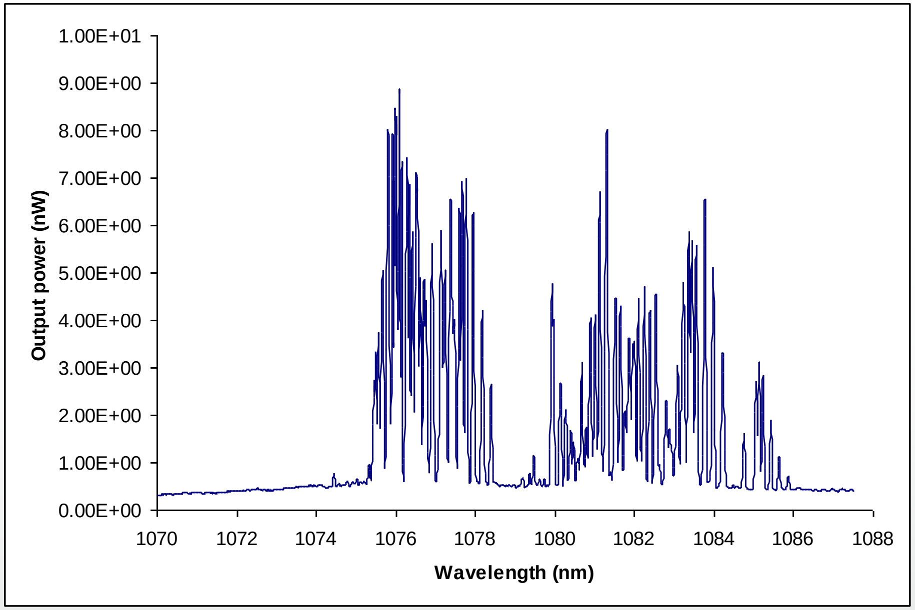


Fluorescent spectrum from GLS microsphere doped with 1.5mol% Nd. Inset, close up on WGM. This measurement was taken using a fibre coupled microsphere.

Initial Lasing Observations



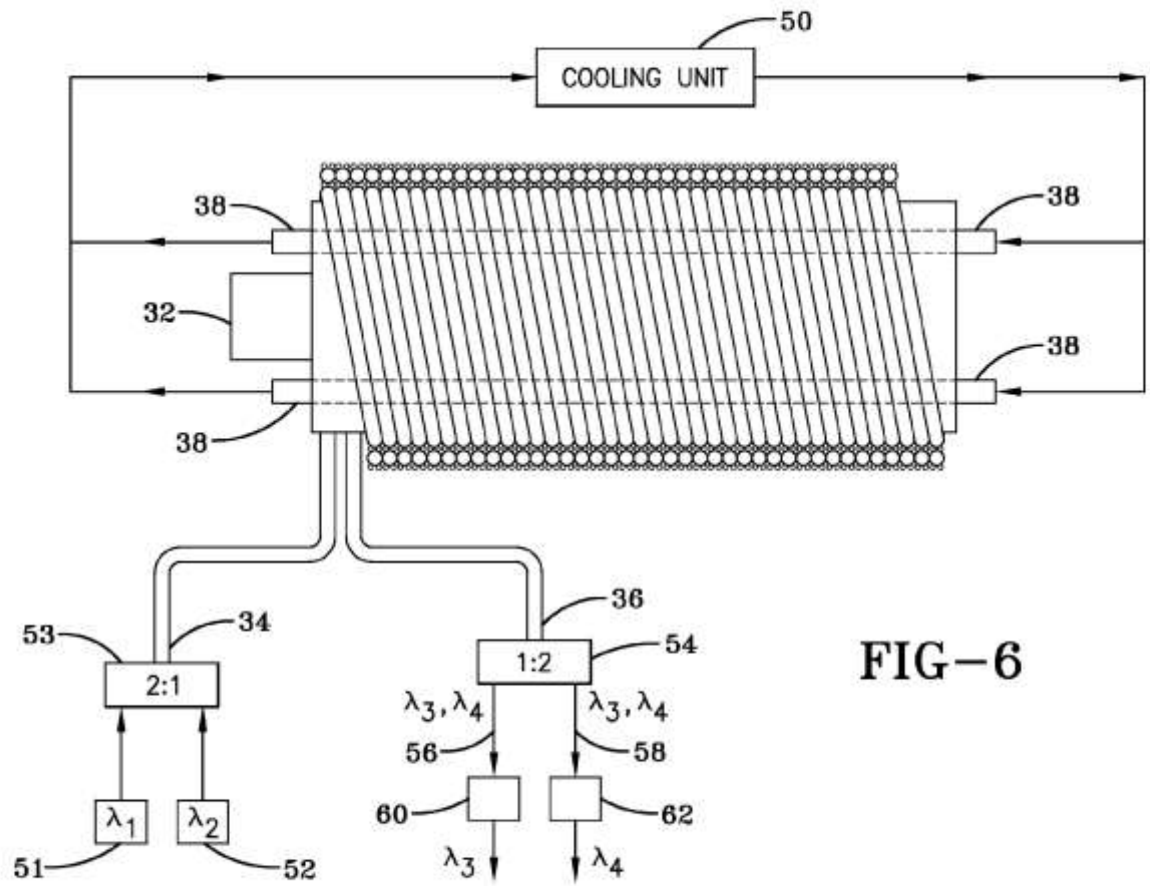


217 mW Pump Power

Maximum Pump Power

Laser Threshold: 82 mW delivered to sphere

(19) **United States**
(12) **Patent Application Publication** (10) **Pub. No.: US 2008/0212620 A1**
ABDELDAYEM (43) **Pub. Date: Sep. 4, 2008**



FIG−6

UV-Vis-NIR Spatial Beam Combination

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First ever defence application ...

Siege of Syracuse
2nd Punic War - 214 BC

Burning Mirrors of Archimedes

Courtesy of Prof M. Zervas

Characteristics of Microsphere Lasers

- Extremely low threshold
- Simple, robust cavity, easily fabricated
- Integratable with planar or fibre technology
- Potential for new wavelengths in IR

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Application of Phase Change in Nanophotonics

http://www.nanophotonics.org.uk/

- Plasmonics
- Metamaterials

Active Plasmonics
… The Concept

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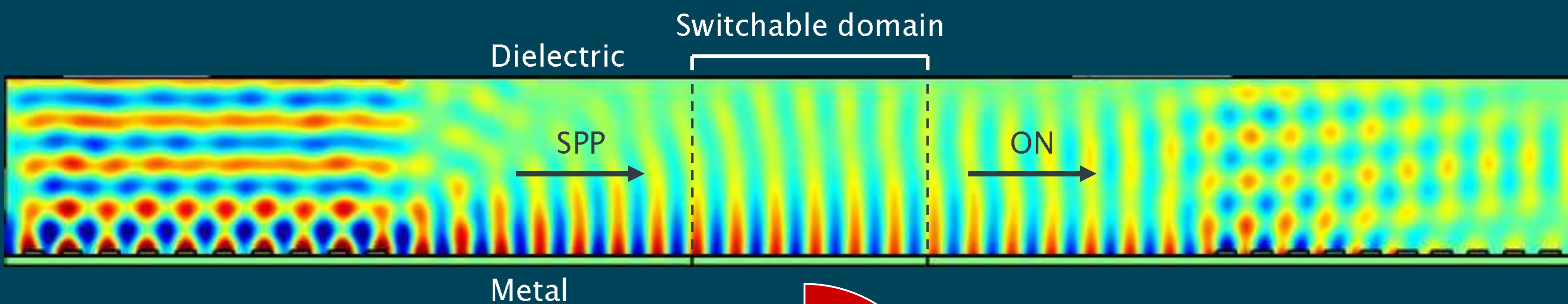

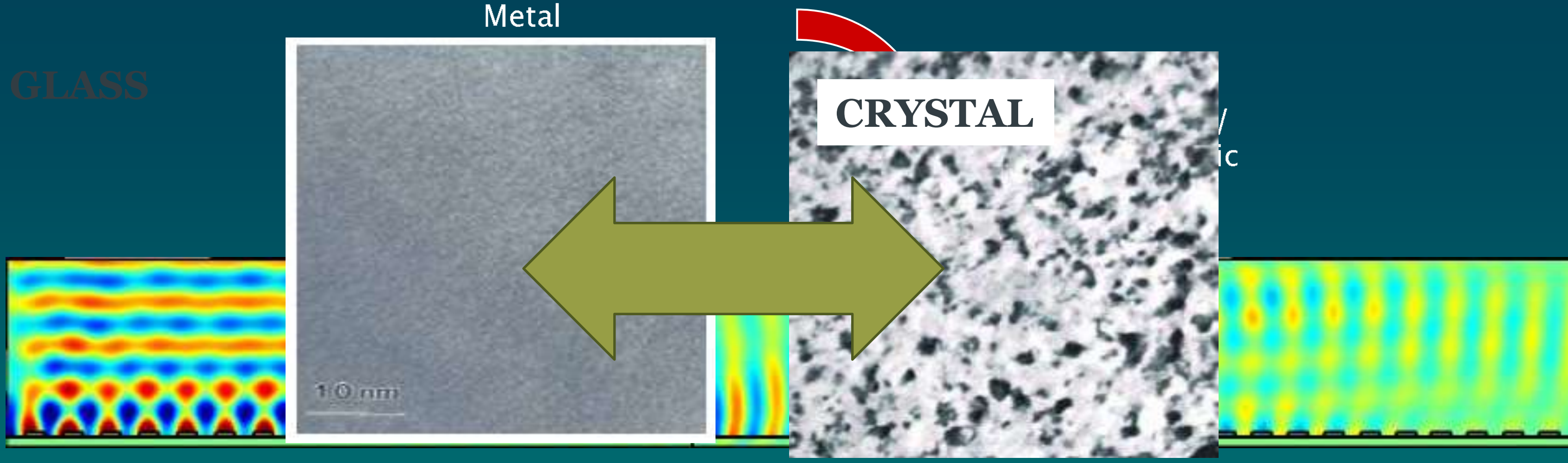

Transient changes in waveguide properties control SPP propagation.

APL **84**, 1416 (2004)

- Short-range atomic order
- Low free electron density
- High activation energy
- High resistivity
- Transparent

- Long-range atomic order
- High free electron density
- Low activation energy
- Low resistivity
- Opaque

Ga-La-S Plasmonics

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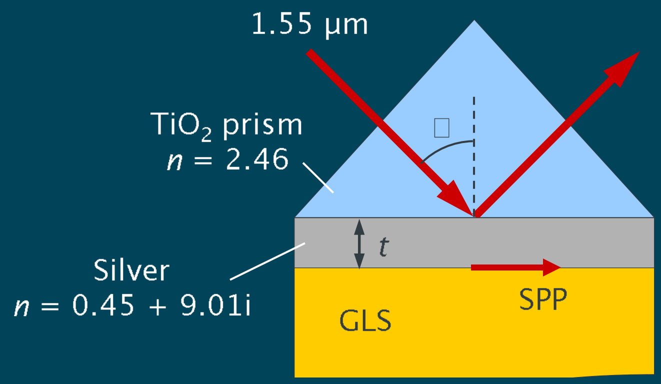
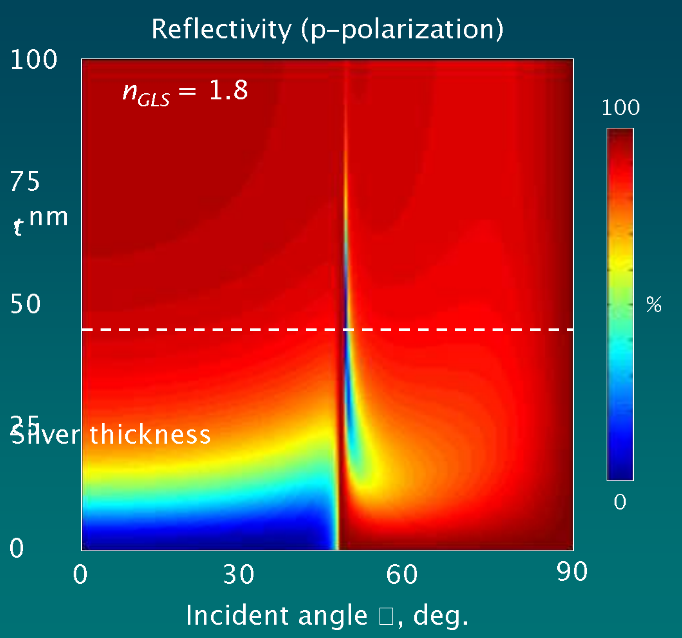
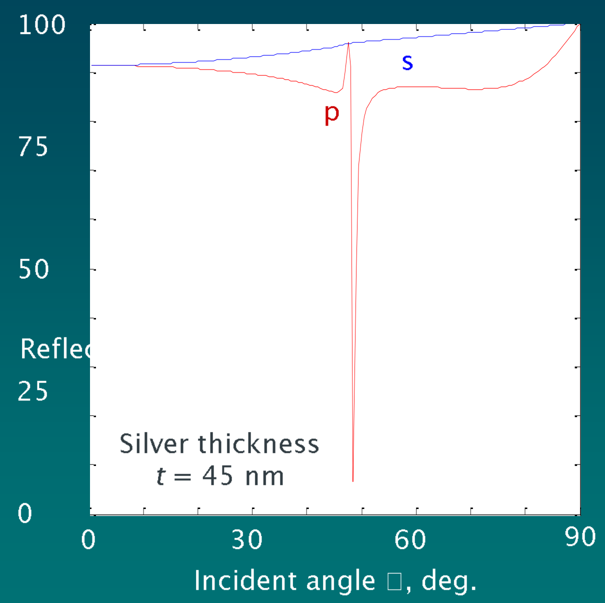
Ge-Sb-Te (GST) unsuitable for plasmonics
- high index
- highly absorbing)

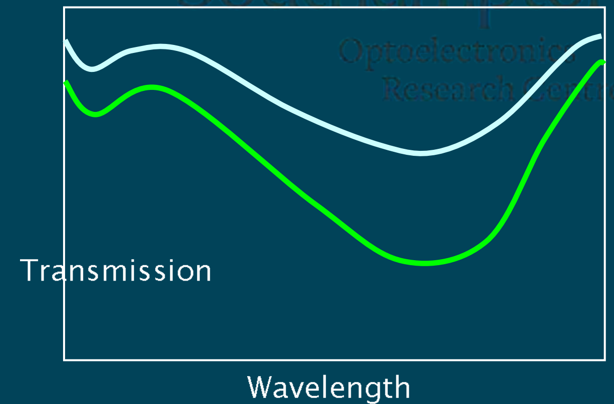
Ga-La-S is much better:
- transparent above ~700 nm
- High damage threshold
- Easily polished and coated
- non-toxic



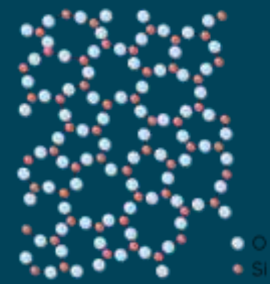




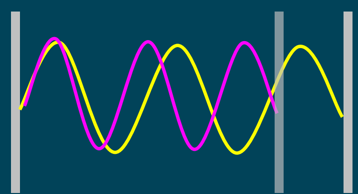
Resonance switching

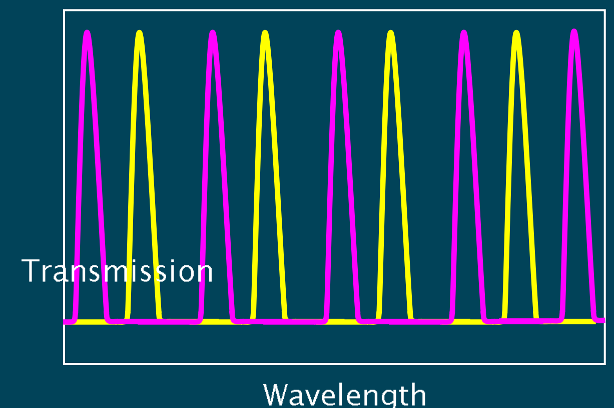


Nonlinear Medium



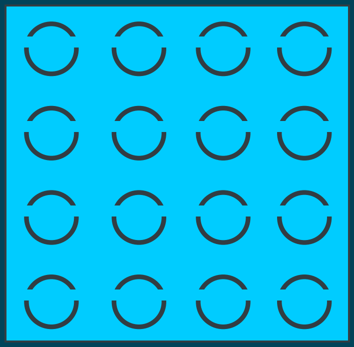
Fabry-Perot Resonator

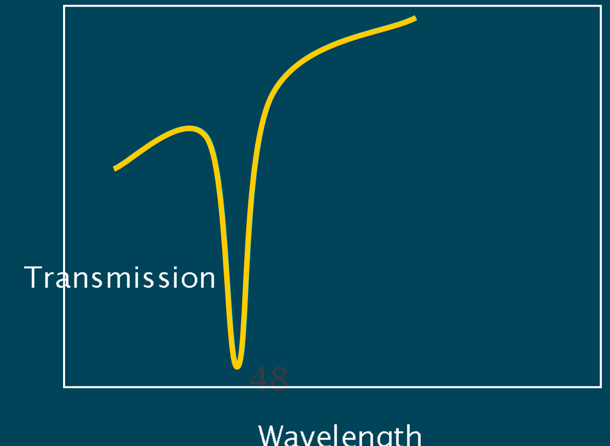




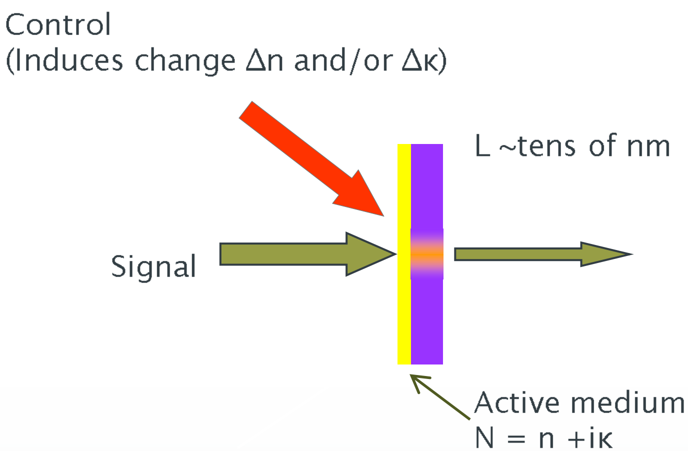
Can we switch our metamaterials?

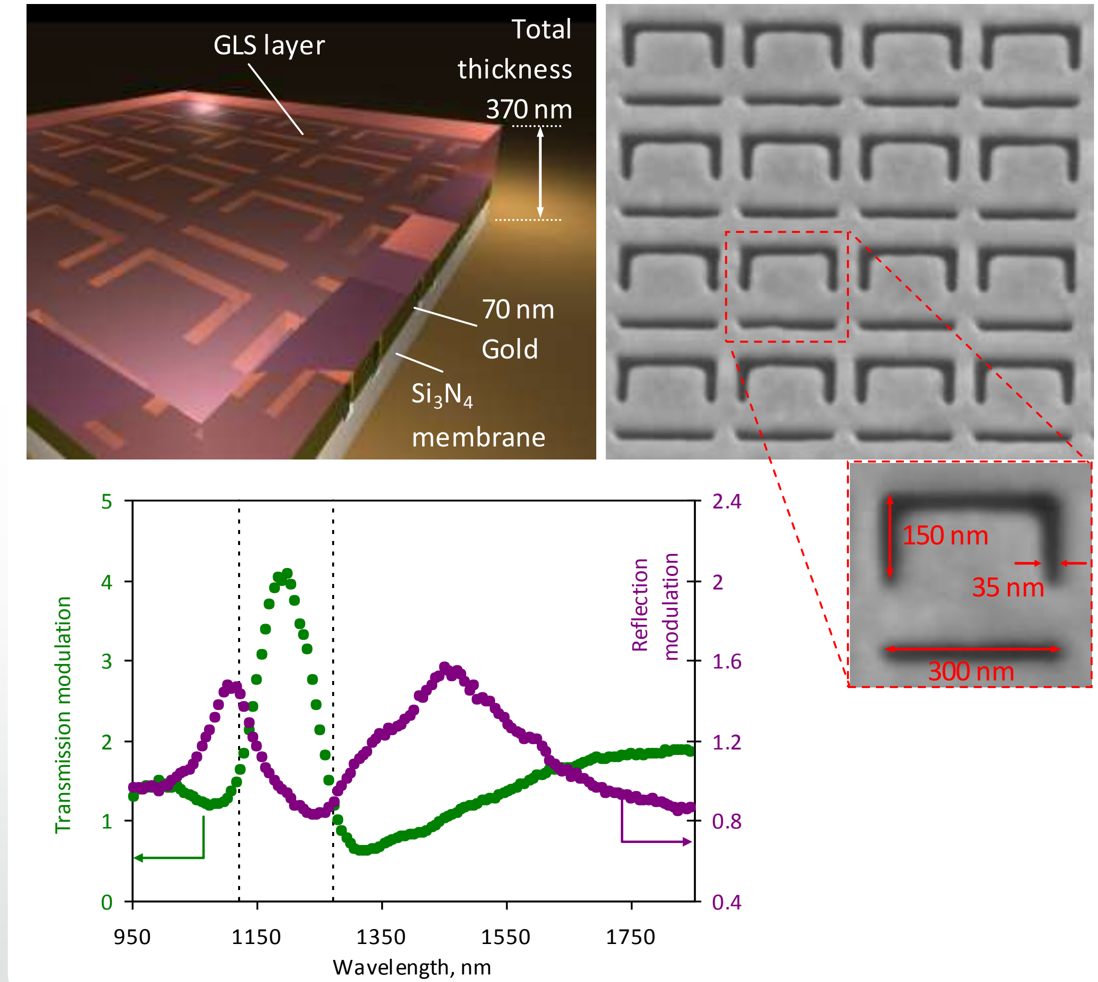
Planar Metamaterial





Chalcogenide metamaterial hybrid: Electro-optic modulator





Gallium Lanthanum Sulphide:

- Optically/electrically-induced threshold switching: amorphous – crystalline
- Transmission contrast 4:1 in a device only $^1/_3$ of a wavelength thick.
- Operational band tuneable by design across VIS-IR range

Sámson, et al., Appl. Phys. Lett. ***96,*** *143105 (2010)*

Concluding Remarks

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- Purify, purify, purify
- Don’t (always) blame the composition
- Consider other geometries, emerging technologies
- Collaborate openly* (or find a very wealthy sponsor)
- Learn from history

Four years later....

*when you can

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First ever defence application …

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